



NATO Security through Science Series - A:
Chemistry and Biology

Hydrogen Materials Science and Chemistry of Carbon Nanomaterials

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 Springer



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Hydrogen Materials Science and Chemistry of Carbon Nanomaterials

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Series A: Chemistry and Biology

Hydrogen Materials Science and Chemistry of Carbon Nanomaterials

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PREFACE

The 2005 International Conference “Hydrogen Materials Science and Chemistry of Carbon Nanomaterials” (ICHMS’2005) was held in September 5-11, 2005 in the remarkable city Sevastopol (Crimea, Ukraine) known for its heroic and unusual fate. In the tradition of the earlier ICHMS conferences, this 9th ICHMS’2005 meeting served as an multidisciplinary forum for the presentation and discussion of the most recent research on transition to hydrogen-based energy systems, technologies for hydrogen production, storage, utilization, materials processing and chemical behavior, energy and environmental problems. The aim of ICHMS’2005 was to provide the wide overview of the latest scientific results on basic research and technological applications of hydrogen interactions with metals and other materials. The active representatives from industry, research/academic organizations and governmental agencies could meet, discuss and present the most recent advances in hydrogen concepts, processes and systems, to evaluate current progress and to exchange academic information, to identify research needs and future development in this important area. This conference should help further the progress of hydrogen-based science and promote the role of hydrogen in the energy field.

The ICHMS’2005 was the conference, where a related new important topic of considerable current interest on fullerene-related materials as hydrogen storage was included into the conference program. This meeting gave an opportunity for researchers to cover the entire range of basic and applied materials focusing on synthesis, structure, properties and applications of diverse carbon materials ranging from nanotubes and fullerenes to carbon fiber composites and sorbents. Papers on related topics and studies devoted to new methods, modelling, theory, computational simulation, design, experimentation and measurement were welcome. Thus, the ICHMS’2005 conference was unique in bringing together hydrogen and carbon materials researchers, scientists, engineers and practitioners from developed countries of Europe and America, new independent states of FSU and other countries for discussions in advanced materials development and applications.

The ICHMS’2005 format consisted of invited lectures, oral and poster contributions and also the conference representatives took part in the exhibition of new materials and equipment.

By attending this conference, the audience gained an insight into the current status of research and development in academia, national laboratories, industries in the field of metal-hydrogen systems and carbon nanomaterials and had the opportunity to develop collaborations between presenters.

This book with ICHMS’2005 Proceedings brings together the research papers of invited and contributed speakers. We hope that they will serve as both a useful reference and resource material for all the participants and for those whose interest in the subject matter may develop after the event.

Finally, this conference was generously supported by the Scientific and Environmental Affairs Division of NATO as an Advanced Research Conference within the Physical and Engineering Science and Technology Area of the NATO Science Programme. Their contribution is gratefully acknowledged and the

Organizing and all ARW participants want to overflow with effusive thanks to NATO Committee for the financial support of our 9th ICHMS'2005 Conference and to **Mr. Jean Fournet**, Assistant Secretary General, Chairman of NATO Science Committee, and **Mr. Fausto Pedrazzini**, Programme Director, NATO Scientific Affairs Division, for the displayed mutual understanding and the comprehension of significance of problems under discussions at the ICHMS'2005 conference.

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international association for hydrogen energy

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WELCOME TO THE PARTICIPANTS OF ICHMS'2005

In the last two years, there has been a speeding up in the Hydrogen Energy related activities and towards Hydrogen Economy. In the summer of 2003, the United States has started international cooperation through binational agreements in Hydrogen Energy Technologies. The European Union has earmarked a large Budget in order to stimulate Hydrogen Energy R&D activities. The Japanese WE-NET Program, which started earlier in 1995, is growing with more and more international projects between Japanese and overseas R&D organizations.

The United Nations Industrial Development Organization (UNIDO), which has been established to better and improve the living conditions around the world and especially in developing countries through industrial development, has seen the great potential of Hydrogen Energy for the betterment of economical and environmental conditions around the world, and has decided to establish an International Centre on Hydrogen Energy Technologies (ICHET) to help convert the world to Hydrogen Economy and coordinate the related activities. Studies were carried out to determine the most suitable and/or convenient location for the Centre. It was decided that the Centre should be located somewhere between the industrial countries and the developing countries, and should be easy to reach from around the World. Consequently, it was agreed that such a location could be Istanbul, Turkey, located between the three continents.

UNIDO-ICHET began operations in May 2004. It has started developing two Databanks. The first Databank will cover the R&D organizations in the world, and their research activities and publications. The second Databank will cover the Hydrogen Energy related industries, their products, specifications and prices. Both Databanks will be updated every month. The Centre also started establishing Hydrogen Energy Pilot Projects around the world. In four continents, some ten projects have already been started, using hydrogen produced from such renewable energy sources as hydro, wind and geothermal energy to meet the fuel needs of various communities. The Centre is conducting negotiations to initiate other Pilot Projects. These will all help to speed up the conversion to the Hydrogen Energy System.

International conferences, such as the ICHMS'2005, will help speed up this transformation. At the conference, recent research findings on hydrogen materials science and metal hydrides chemistry will be presented and discussed. The chemistry of metal hydrides and hydrogen materials science will play an important role in hastening the conversion to the Hydrogen Economy. The research endeavors of the scientists and engineers participating in this conference will make significant contributions to facilitate this milestone conversion.

I take this opportunity to congratulate the organizers of this important series of International Conferences on Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, and wish all of the participants a very productive conference and pleasant days in the beautiful Crimea.

T. Nejat Veziroglu
Honorary Chairman, ICHMS'2005
President, Int. Association for Hydrogen Energy
Director, UNIDO-ICHET



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Dear Colleagues !

On behalf of Association for Hydrogen Energy in Ukraine we are glade to welcome everybody at international conference ICHMS'2005 that became rather known.

Three decades have passed since the inception of hydrogen-energetic movement in the seventies. Having started with a small group of enthusiasts, the hydrogen movement turned into a large international force supported by governments, large industrial firms and United Nations Organizations. The organization under the aegis of UNIDO, International Centre on Hydrogen Energy Technologies (ICHET), in Turkey has become a huge victory of the world-wide hydrogen movement.

Scientists from the most of developed countries that work in the field of hydrogen energy are united within the bounds of International Association for Hydrogen Energy and National Associations.

Based on Organization Committee ICHMS, Association for Hydrogen Energy was also established in Ukraine a year ago. The Association sets itself as an object to spread knowledge about the necessity of introducing hydrogen energy among population, to discuss tasks, problems and difficulties related to the conversion of energetic system into hydrogen energy in mass media.

We hope Association for Hydrogen Energy under support of International Association for Hydrogen Energy and with Organization Committee of International conference "Hydrogen Materials Science and Chemistry of Carbon Nanomaterials" will be able to enlarge the circle of supporters of hydrogen energy in Ukraine, to draw industry and Government in solving these problems.

We are sure that in the near future achievements of scientific groups in Ukraine and all over the world will allow the transformation of the Crimea peninsula into the ecologically pure region of Ukraine that will be able to become the region of hydrogen transport and technologies after the example of already existing hydrogen regions in America and Europe.

We invite enthusiasts of the hydrogen future to support Association for Hydrogen Energy in its aspiration for making Ukraine purer and more energetically independent State.

Taking the opportunity, we congratulate all delegated of the conference on so important event, on the beginning of the work of ICHMS'2005 conference.

On behalf
of members of AHEU

Schur D.V.
Zaginaichenko S.Yu.
Adejev V.M.



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Dear participants and guests of ICHMS'2005 Conference!

As President of National Academy of Sciences of Ukraine, receiving at its soil so big collective of scientists from different countries, I want to congratulate You on opening of regular forum.

Harnessing advanced achievements of science, technique and technology, the mankind steadily moves forward in its development. However, the problems associated with ecology and efficient use of regenerated power sources were of secondary importance for a time. Chernobyl disaster is the warning to the World Community. It exposed the need for near-term development, manufacturing and commercial utilization of environmentally friendly types of power.

One of the most important as well as the most ecologically pure power source is hydrogen, that constitutes the heart of hydrogen power engineering and considered as a future alternative to fossil power sources.

Among the main directions a due attention should be given to the investigation and development of the crucially new materials for hydrogen power engineering, adjustment of their manufacturing technologies, design of devices, methods and measures, running these processes, as well as to organization of undertakings on implementation of the above listed tasks in commercial production.

For now, the scientific institutions and production facilities of Ukraine have managed to save their previously accumulated experience in developing new hydride materials and their manufacturing technologies.

The problems, associated with the development and utilization of new ecologically pure power technologies are the common ones both for Ukraine and humanity.

One of the objectives is to provide an international forum for the scientists and researchers, working in the field of ecologically pure power systems, hydride forming materials and environmental problems, to share the ideas and results of the update elaborations, technologies and experiments, targeted on the practical embodiment. We believe, the Conference will be a guideline for planning and development of economically justified alternative power systems and storage systems on the basis of metal hydrides.

In summary, I would like to wish Conference Participants and all scientists, involved in these subjects, success in your so much needed and fruitful activity.

Academician B.E. Paton

***PRESIDENT OF NATIONAL
Academy of Sciences of Ukraine***

Russian Academy of Science



The energy arteries of the corporate body of mankind are still fed mainly by fossil fuels; but they are in danger of running dry soon unless new energy sources are made available. Of the possible candidates, hydrogen promises to be the ultimate energy carrier -to replace oil and natural gas. One of most efficient ways in which hydrogen may be utilized for this purpose is offered by the metal-hydrogen systems.

Hydriding metals, alloys, nanocarbon and composite materials can store hydrogen safely at relatively low pressures and temperatures. Very many other applications are also possible - such as heating and cooling, waste heat storage, pumping, pressurizing, heat-pumping, hydrogen purifying, deuterium separation, electricity production, etc.

As a source of 'clean' energy, hydrogen is also going to be the permanent answer to another global problem caused by utilization of fossil fuels, such as the greenhouse effect, climate change, acid rains, ozone layer depletion, pollution and oil spills.

The chemistry of carbon nanomaterials and hydrogen materials science will play an important role in hastening the conversion to the Hydrogen Energy System. International conferences like ICHMS'2005 help speed up this conversion. The previous eight Conferences of this series navigated by the National Academy of Sciences of Ukraine gathered together a rapidly increasing number of scientists, engineers and students from Ukraine and neighbouring countries of Europe and Asia and from the US. The Conference evidently got one of the most representative forums for hydriders from all over the world.

I take this opportunity to congratulate the organizers of this important series of International Conferences on Hydrogen Materials Science and Chemistry of Carbon Nanomaterials and wish all of the participants a very productive conference and pleasant days in the beautiful Crimea.

Academician
Yu.A. Ossipyan



TO PARTICIPANTS OF IX INTERNATIONAL CONFERENCE “HYDROGEN MATERIALS SCIENCE AND CHEMISTRY OF CARBON NANOMATERIALS”

Dear friends !

I am honored to welcome you on behalf of the Georgian Academy of Sciences.

Hydrogen energy is the future of Mankind. The ideal hydrogen-cycle represents a really renewable energy source, which utilize the nontraditional energy sources (such as, for example, solar energy, wind-energy), and does not depend on the expendable treasures of the soil - coal, oil, or gas.

Georgia is a mountainous country rich in water-power. Nevertheless, the energy supply of our country can not be built exclusively upon the set of hydroelectric stations. Creation of a small number of big power-stations accompanied by an extensive electricity supply network seems to be economically effective, but the same economical factors applied to the electricity supply schemes can provide destruction of the set of mountainous little villages.

In contrast, the hydrogen energy-cycle implying combinations of a local water-source with local solar-, wind- or hydro-energy plants, can be realized separately in each village. Thus, foundation of the system of local hydrogen-energy-cycles can be considered as a main condition for the stable development of mountainous regions.

One of the chief points in the hydrogen-energy-cycle is the problem of hydrogen storage. Metal hydrides and carbon nanomaterials are considered today as the most acceptable compounds for hydrogen safety accumulation. Fundamental investigations of metal hydrides began in Georgia at the end of 60th in E.Andronikashvili Institute of Physics. Simultaneously in the Caucasus Institute of Raw Materials (“KIMS”) were studied very actual problems of hydrogen delivering from different natural compounds. The hydrogen energy problems still keep the keen interest of Georgian researchers.

Direct contacts between the scientists stimulate the progress of sciences, and scientific collaboration produces the friendship of nations. We welcome the collaboration of scientists aimed to the increase of security, good health and prosperity of peoples.

We wish many scientific achievements and happiness to participants of IX International Conference “Hydrogen Materials Science and Chemistry of Carbon Nanomaterials” (ICHMS’2005) in Crimea. Good luck to the conference organizers.

Thomas V. Gamkrelidze
Academician,
President of the Georgian Academy of Sciences



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**Dear colleagues, ladies and gentlemen,
participants of 9th International conference “Hydrogen materials
science and chemistry of carbon nanomaterials” !**

Every time ICHMS conference get together scientists from many countries of the world, who are engaged in the always urgent problems of humanity such as a search for new forms of energy and materials science.

The progress of civilization is impossible without powerful energetics and the further development of power engineering is impossible without changing classical fossilized energy sources (gas, petroleum, coal) to alternative, in particular to hydrogen energetics.

The conversion to the hydrogen energy system will release the world from the gas-petrol dependence, save the environment from pollutions caused by the use of fossil fuels.

In this connection the research and application of materials capable of interacting actively with hydrogen, its accumulating and storing will be of the utmost significance. This is of particular actuality for creation of mobile energy sources both for mobile telephones and for hybrid electric cars that are developed by all large car manufacturers of the world. In this connection the hydrogen capacity of carbon nanostructural materials, such as fullerenes, nanotubes, nanofibers and other nanostructures, has aroused a special interest of researchers.

In the course of further development of science and technologies the whole world community will get a new level of services based on achievements of modern science.

At the ICHMS'2005 conference scientists will be able to represent the latest elaborations in the field of hydrogen materials science and carbon nanomaterials, to exchange the results of investigations and to sum up the two-year work.

STCU renders a financial support for many projects that solve the above problems and supports ICHMS conferences more than 10 years. Taking the given opportunity, I should like to congratulate all delegates of this conference upon the regular forum.

Boris A. Atamanenko
Senior Deputy of
STCU Executive Director

Dear colleagues!

The basic current energy carriers (oil, gas, coal, uranium) unfortunately possess two insuperable disadvantages: they are non-renewable and it is almost impossible to make them ecologically clean.

The major alternative to these carriers includes solar energy (in its different forms), thermonuclear energy and hydrogen energy. Both solar and thermonuclear energy can be used in the future as effective power sources for stationary applications (for example, residence homes, railway stations and production facilities). However, for mobile applications, such as cars, airplanes, etc., utilization of these sources is highly problematic. And this is where hydrogen can play a major role! Hydrogen is the most abundant element on Earth and it forms pure water when reacting with oxygen. Besides, burning hydrogen in fuel cells allows generating electric power with nearly 100% efficiency.

On one hand, it sounds nice and easy – just get hydrogen from water and use it wherever the need is. However, in reality it is not so easy, although within certain limits this idea works perfectly. The major problem appeared to be how to store hydrogen in compact form, since it has very low density and its boiling point is only 21 K.

In the beginning, it seemed like the possible way to solving this problem is by facilitating chemical reactions, primarily hydrogenation of metals. However, decades of intensive search in this direction did not produce expected results. Accordingly, alternative methods began to appear and a number of studies in this field sharply increased. From this perspective, it was important to coordinate and combine efforts of the researchers worldwide as well as create an opportunity for them to periodically meet and discuss their results in order to select the most promising ways and avoid dead ends.

International Conferences on Hydrogen Material Science (ICHMS), which have been held on a regular basis for the last almost 20 years, represent one of the major forums allowing scientists to discuss theoretical and practical issues associated with hydrogen energy. The importance of these meetings is hard to overestimate. Besides, such conferences attract attention of mass media and general public, which is very important in terms of adopting economic decisions at the level of governments of interested countries.

I would like to take this opportunity to thank the organizers of these conferences for their contribution to creating and strengthening collaboration between scientists from different countries in the field of hydrogen energy and wish the ICHMS a success in September 2005!

Raouf O. Loutfy

**President,
MER Corporation**

THE PECULIARITIES OF HYDROGENATION OF PLATINUM FULLERIDES

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Abstract. The statistical theory of processes of phase transformations realized by hydrogenation of metalfulleride has been developed in present paper. Such reaction was studied experimentally for fullerides of palladium and platinum [1, 2].

For solving the problem the free energies f_i ($i = 1, 2, 3$) of respective ΦPt , ΦPtH_x , ΦH_x phases have been calculated using the average energies method, their dependences on temperature, the c_1 , c_2 , x concentrations of C_{60} , C_{70} fullerenes and hydrogen, the order parameter η in distribution of fullerenes over the lattice sites and energetic constants have been defined.

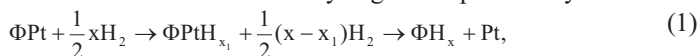
The plots of free energies of ΦPt , ΦPtH_x , ΦH_x phases have been constructed as a function of concentration for different temperatures. The phase diagram has been constructed by intersection points of these plots and with the use of method of total tangent lines to them. This diagram defines the temperature and concentration regions of forming of all phases of chemical reaction.

Keywords: hydrogen solubility, hydrofullerite and hydrofulleride of platinum, phase diagram

1. Introduction

The experimental investigation of chemical reactions in fullerite-metal-hydrogen systems makes possible the problem solution of effective storage of hydrogen as ecologically clean energy source. Metalfullerides are the most promising materials in this respect, because they allow one to increase the sorptional capacity of hydrogen fullerite, to raise the rate of their hydrogenation, to reduce the hydrogenation temperature and to eliminate the other side reactions [1-9]. In this case the hydrogen concentration in hydrofullerites and fullerides hydrides may run to 7,7 mass.% [10, 11]. At hydrogenation the structure of initial crystals retained, only the parameter of crystal lattice is increased [12-14].

In the case of platinum the chemical reaction of hydrogenation proceeds by the scheme:



where $\Phi = \text{C}_{60}, \text{C}_{70}$. At first, the hydrofulleride ΦPtH_x is formed over the temperature range of 400-550 K, thereafter with increased temperature in the range from 600 to 700 K the formation of hydrofullerite phase ΦH_x occurs and the separation of pure platinum takes place [15].

The development of statistical theory of processes of phase transformations realized by hydrogenation of metalfulleride, the elucidation and substantiation of conditions of proceeding reaction (1) are of more direct interest to scientists. The atomic configuration model of crystals is used below without considering possible processes in subsystems of interstitial atoms as hydrogen and platinum.

2. Setting up a problem

For solving the defined problem the free energies f_i ($i=1,2,3$) of respective ΦPt , ΦPtH_x , ΦH_x phases have been calculated by the method of average energies [16], their dependences on temperature T , the c_1, c_2, x concentrations of $\text{C}_{60}, \text{C}_{70}$ fullerenes and hydrogen, the order parameter η in distribution of fullerenes over the lattice sites and energetic constants have been determined. The simplified approximations have been taken in calculations. The fcc lattice of L1_2 type [17] is proposed to be geometrically ideal. The concentration of fullerenes $\Phi_1 = \text{C}_{60}$, $\Phi_2 = \text{C}_{70}$ can be any one over the interval $[0; 1]$ [18-23]. The interactions between fullerenes, platinum and hydrogen atoms are taken into consideration for the nearest neighbours and in this case the approximation of spherically symmetric rigid balls is assumed [24, 25]. The correlation in substitution of sites and interstitial sites by fullerenes and atoms of platinum and hydrogen is not taken into consideration. The ordering of fullerenes Φ_1, Φ_2 is taken into account by the Cu_3Au type. The orientational ordering in fullerite was studied experimentally [26-30]. It is expected also that the arrangement of platinum and hydrogen atoms takes place in interstitial sites of crystal lattice of fullerite. Taking into consideration that radiuses of H and Pt atoms and $\Phi = \text{C}_{60}, \text{C}_{70}$ molecules are equal to 0.46; 1.3875; and 7.1 Å respectively, it is assumed that platinum atoms are arranged in octahedral O interstitial sites (of greater volume) of ΦPt , ΦPtH_x phases and hydrogen atoms occupy the tetrahedral θ and trigonal Q positions in the ΦPtH_x phase, in which they form the hydrogen dumb-bells along the spatial diagonals of cubic cell of fullerite crystal. The disposition of hydrogen atoms in octahedral O interstitial sites can be nonequilibrium by virtue of their sizable volume, several hydrogen atoms can arrive at octahedral interstitial sites. Because of this, it is suggested that in the ΦH_x phase the hydrogen atoms occupy the tetrahedral and trigonal interstitial sites forming the dumb-bells along the spatial diagonals of cube of fullerite elementary cell. Several hydrogen atoms find themselves in the octapositions and make up the dumb-bells along the axes x, y, z parallel to edges of lattice cell volume, i.e. in octahedral interstitial sites the hydrogen clusters (D_1, D_2 positions) are formed, as shown in Fig. 1.

3. Theory

We calculate the free energies of phases of chemical reaction (1) for the following investigation and comparison at different temperatures for the purpose of phase diagram construction.

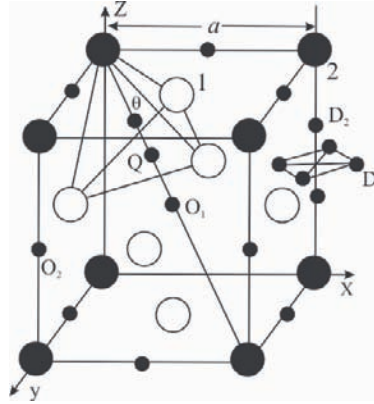


Figure 1. The fcc lattice of $L1_2$ hydrofullerite.

○● – the sites of first and second type of Φ_1, Φ_2 fullerenes,

● – the interstitial sites (octahedral O_1, O_2 , tetrahedral Θ , trigonal Q and clasteral D_1, D_2).

At the temperatures of each chemical reaction execution the free energies of corresponding phases are equal. The free energies of phases undergo a change with temperature and components concentration and the phase with lesser value of free energy will be realized. The free energy of gaseous hydrogen (the less value) is ignored in calculations.

The free energy of i -phase ΦPt , ΦPtH_x , ΦH_x , Pt respectively is calculated by formula:

$$F_i = E_i - kT \ln G_i - kTN_H \ln \lambda \quad (i = 1, 2, 3, 4), \quad (2)$$

where E_i is internal configuration energy of these phases defined by the sum of energies of paired interaction between the nearest atoms of hydrogen, platinum and molecular Φ_1, Φ_2 , G_i is thermodynamic probability of distribution of hydrogen, platinum atoms and fullerenes over all positions of crystals determined according to the rules of combinatorics, k is Boltzmann's constant, T is absolute temperature, N_H is the number of hydrogen atoms, λ is their activity. The last summand of formula (2) appears is the expressions for free energies of the ΦPtH_x and ΦH_x phases containing the hydrogen.

We also introduce the following designation:

N is the number of all sites (fullerenes) of the crystal, $N_1=3N/4$, $N_2=N/4$ are the numbers of sites of the first and the second types legal for fullerenes Φ_1, Φ_2 , respectively, N_O, N_Θ, N_Q, N_D are the numbers of interstitial sites, octahedral O , tetrahedral Θ , trigonal Q and clasteral D .

The octahedral and clasteral interstitial sites are subdivided into interstitial sites of two types O_1, O_2 and D_1, D_2 depending on their surroundings by the sites of the first and second type:

$$N_O = N, \quad N_\Theta = 2N, \quad N_Q = 2N, \quad N_D = 6N, \quad (3)$$

$$N_{O_1} = \frac{3}{4}N, \quad N_{O_2} = \frac{1}{4}N, \quad N_{D_1} = \frac{9}{2}N, \quad N_{D_2} = \frac{3}{2}N, \quad (4)$$

N_{Φ_1}, N_{Φ_2} are the numbers of Φ_1, Φ_2 fullerenes in each phase ($\Phi\text{Pt}, \Phi\text{PtH}_x, \Phi\text{H}_x$),
 $c_1 = N_{\Phi_1} / N, c_2 = N_{\Phi_2} / N$ are concentrations of Φ_1, Φ_2 fullerenes,
 $N_{\Phi_1}^{(1)}, N_{\Phi_1}^{(2)}, N_{\Phi_2}^{(1)}, N_{\Phi_2}^{(2)}$ are the numbers of Φ_1, Φ_2 fullerenes in the sites of the first and second types:

$$N_{\Phi_1} = N_{\Phi_1}^{(1)} + N_{\Phi_1}^{(2)}, N_{\Phi_2} = N_{\Phi_2}^{(1)} + N_{\Phi_2}^{(2)}. \quad (5)$$

$P_{\Phi_1}^{(1)}, P_{\Phi_1}^{(2)}, P_{\Phi_2}^{(1)}, P_{\Phi_2}^{(2)}$ are a priori probabilities of the substitution of sites of the first and the second types by Φ_1, Φ_2 fullerenes

$$P_{\Phi_1}^{(1)} = N_{\Phi_1}^{(1)} / N_1, P_{\Phi_1}^{(2)} = N_{\Phi_1}^{(2)} / N_2, P_{\Phi_2}^{(1)} = N_{\Phi_2}^{(1)} / N_1, P_{\Phi_2}^{(2)} = N_{\Phi_2}^{(2)} / N_2. \quad (6)$$

The degree of crystal ordering is defined by the order parameter:

$$\eta = 4(P_{\Phi_1}^{(1)} - c_1). \quad (7)$$

Then probabilities $P_{O_i}^{(i)} (\hat{O}_1 = \hat{O}_1, \hat{O}_2, i=1,2)$ are defined by the relations:

$$P_{\Phi_1}^{(1)} = c_1 + \frac{1}{4}\eta, P_{\Phi_1}^{(2)} = c_1 - \frac{3}{4}\eta, P_{\Phi_2}^{(1)} = c_2 - \frac{1}{4}\eta, P_{\Phi_2}^{(2)} = c_2 + \frac{3}{4}\eta. \quad (8)$$

$N_p^{(O_1)}, N_p^{(O_2)}$ are the numbers of platinum atoms in O_1, O_2 interstitial sites, N_H is the number of hydrogen atoms in each phase ΦPtH_x and ΦH_x , c is the concentration of hydrogen atoms relative to the number of interstitial sites:

$$c = N_H / (N_{\Theta} + N_Q) = N_H / 4N \quad \text{for the } \Phi\text{PtH}_x \text{ phase}, \quad (9)$$

$$c = N_H / (N_{\Theta} + N_Q + N_D) = N_H / 10N \quad \text{for the } \Phi\text{H}_x \text{ phase}. \quad (10)$$

At the random arrangement of hydrogen atoms over interstitial sites their numbers in different positions are equal to, respectively:

$$N_H^{(\Theta)} = cN_{\Theta} = 2Nc, N_H^{(Q)} = cN_Q = 2Nc \quad \text{for the } \Phi\text{PtH}_x \text{ phase}, \quad (11)$$

$$N_H^{(\Theta)} = cN_{\Theta} = 2Nc, N_H^{(Q)} = cN_Q = 2Nc, N_H^{(D)} = cN_D = 6Nc, \quad (12)$$

$$N_H^{(D_1)} = cN_{D_1} = \frac{9}{2}Nc, N_H^{(D_2)} = cN_{D_2} = \frac{3}{2}Nc \quad \text{for the } \hat{O}\text{H}_x \text{ phase}.$$

x is the concentration of hydrogen atoms relative to the number of sites (fullerenes) of crystal lattice:

$$\begin{aligned} x &= 4c \quad \text{for the } \Phi\text{PtH}_x \text{ phase}, \\ x &= 10c \quad \text{for the } \Phi\text{H}_x \text{ phase}. \end{aligned} \quad (13)$$

4. Fulleride ΦPt . Calculation of free energy

Free energy of fulleride is calculated with regard to the interaction of nearest pairs $\Phi_1\Phi_1, \Phi_2\Phi_2, \Phi_1\Phi_2, \Phi_1\text{Pt}, \Phi_2\text{Pt}$, taking that fullerenes are distributed in lattice sites and platinum atoms occupy the octahedral interstitial sites of lattice.

The elementary cell has four sites (three of the first type and one of the second one) and four octahedral interstitial sites (three of the O_1 type and one of the O_2 type).

The interatomic distances are equal to:

$$r = a/\sqrt{2}, \quad r_1 = a/2, \quad (14)$$

where a is the parameter of crystal lattice.

The free energy f_1 for one site of crystal lattice for the ΦPt phase, in view of formulae (8), is found in the form

$$\begin{aligned} f_1 = \frac{F_1}{N} &= (E_1 - kT \ln G_1) / N = \\ &= -6(c_1^2 \upsilon_{\Phi_1\Phi_1} + c_2^2 \upsilon_{\Phi_2\Phi_2} + 2c_1c_2 \upsilon_{\Phi_1\Phi_2}) - \frac{3}{8}(2\upsilon_{\Phi_1\Phi_2} - \upsilon_{\Phi_1\Phi_1} - \upsilon_{\Phi_2\Phi_2})\eta_1^2 - \\ &\quad - 6(c_1 \upsilon_{\Phi_1P} + c_2 \upsilon_{\Phi_2P}) - 6(\upsilon_{\Phi_1P} - \upsilon_{\Phi_2P})\eta_1 + \\ &\quad + \frac{1}{4}kT[3(c_1 + \frac{1}{4}\eta_1)\ln(c_1 + \frac{1}{4}\eta_1) + 3(c_2 - \frac{1}{4}\eta_1)\ln(c_2 - \frac{1}{4}\eta_1) + \\ &\quad + (c_1 - \frac{3}{4}\eta_1)\ln(c_1 - \frac{3}{4}\eta_1) + (c_2 + \frac{3}{4}\eta_1)\ln(c_2 + \frac{3}{4}\eta_1)], \end{aligned} \quad (15)$$

where

$$\begin{aligned} E_1 &= -3N[P_{\Phi_1}^{(1)}(P_{\Phi_1}^{(1)} + P_{\Phi_1}^{(2)})\upsilon_{\Phi_1\Phi_1} + P_{\Phi_2}^{(1)}(P_{\Phi_2}^{(1)} + P_{\Phi_2}^{(2)})\upsilon_{\Phi_2\Phi_2} + \\ &\quad + (2P_{\Phi_1}^{(1)}P_{\Phi_2}^{(1)} + P_{\Phi_1}^{(1)}P_{\Phi_2}^{(2)} + P_{\Phi_1}^{(2)}P_{\Phi_2}^{(1)})\upsilon_{\Phi_1\Phi_2}] - \\ &\quad - \frac{1}{2}N[(1P_{\Phi_1}^{(1)} + P_{\Phi_1}^{(2)})\upsilon_{\Phi_1P} + (1P_{\Phi_2}^{(1)} + P_{\Phi_2}^{(2)})\upsilon_{\Phi_2P}] \end{aligned} \quad (16)$$

is configuration energy of the ΦPt phase,

$$\ln G_1 = -\frac{1}{4}N(3P_{\Phi_1}^{(1)} \ln P_{\Phi_1}^{(1)} + 3P_{\Phi_2}^{(1)} \ln P_{\Phi_2}^{(1)} + P_{\Phi_1}^{(2)} \ln P_{\Phi_1}^{(2)} + P_{\Phi_2}^{(2)} \ln P_{\Phi_2}^{(2)}) \quad (17)$$

is thermodynamic probability of the ΦPt phase, $\upsilon_{\Phi_1\Phi_1}, \upsilon_{\Phi_2\Phi_2}, \upsilon_{\Phi_1\Phi_2}$ are energies of interaction between the mentioned nearest pair of fullerenes with the opposite sign, η_1 is the long-range order parameter in distribution of fullerenes over the sites of the ΦPt crystal lattice.

The derived formula (15) defines the dependence of the free energy for fulleride on the c_1, c_2 concentrations of Φ_1, Φ_2 fullerenes, temperature T , order parameter η_1 and energetic constants. Further we shall investigate the fulleride phase, analyse the calculation results and construct the constitution diagram using this formula (15).

5. Hydrofulleride ΦPtH_x . Free energy

The free energy F_2 of this phase is combined from the free energy F_1 of the ΦPt phase, components defined by interaction between fullerenes and hydrogen atoms and the component estimated by activity of dissolution of hydrogen atoms in this phase.

The elementary cell contains eight tetrahedral interstitial sites of the same type and eight trigonal also the same, arranged on the spatial diagonals (Fig. 1), and hydrogen atoms are distributed over these interstitial sites. Each tetrahedral interstitial site is surrounded by four nearest sites at the distance r' , three of them are of the first type and one of them is of the second type. Trigonal interstitial site has three sites of the first type in the nearest surroundings at the distance r'' , in this case:

$$r' = a\sqrt{3}/4 \approx 0,43a, \quad r'' = a/\sqrt{6} \approx 0,41a. \quad (18)$$

Calculating free energy, we consider interaction at the distance $r' \approx r''$, because the r', r'' values differ little from one another.

The theory proposes that not all interstitial sites Θ and Q are filled with hydrogen atoms, some of them are vacant. At the full occupation of all interstitial sites Θ and Q by hydrogen atoms, the ΦPtH_4 hydrofulleride is formed with a maximum hydrogen content.

Considering formulae (8), (9), (11), we find the free energy for one site of crystal lattice for the hydrofulleride phase as follows:

$$\begin{aligned}
 f_2 = \frac{F_2}{N} &= (E_2 - kT \ln G_2 - kTN_H \ln \lambda) / N = \\
 &= -6(c_1^2 v_{\Phi_1 \Phi_1} + c_2^2 v_{\Phi_2 \Phi_2} + 2c_1 c_2 v_{\Phi_1 \Phi_2}) - \frac{3}{8}(2v_{\Phi_1 \Phi_2} - v_{\Phi_1 \Phi_1} - v_{\Phi_2 \Phi_2})\eta_2^2 + \\
 &+ \frac{1}{4}kT[3(c_1 + \frac{1}{4}\eta_2) \ln(c_1 + \frac{1}{4}\eta_2) + 3(c_2 - \frac{1}{4}\eta_2) \ln(c_2 - \frac{1}{4}\eta_2) + \\
 &+ (c_1 - \frac{3}{4}\eta_2) \ln(c_1 - \frac{3}{4}\eta_2) + (c_2 + \frac{3}{4}\eta_2) \ln(c_2 + \frac{3}{4}\eta_2)] - \\
 &- 6(c_1 v_{\Phi_1 P} + c_2 v_{\Phi_2 P}) - 6(v_{\Phi_1 P} - v_{\Phi_2 P})\eta_2 - \\
 &- c[7(c_1 v_{\Phi_1 H} + c_2 v_{\Phi_2 H}) + \frac{3}{4}(v_{\Phi_1 H} - v_{\Phi_2 H})\eta_2] + \\
 &+ 4kT[c \ln c + (1 - c) \ln(1 - c)] - 4kTc \ln \lambda,
 \end{aligned} \tag{19}$$

where

$$E_2 = E_1(\eta_2) - \frac{1}{2}(N_H^{(\Theta)} + N_H^{(Q)})[(6P_{\Phi_1}^{(1)} + P_{\Phi_1}^{(2)})v_{\Phi_1 H} + (6P_{\Phi_2}^{(1)} + P_{\Phi_2}^{(2)})v_{\Phi_2 H}] \tag{20}$$

is configuration energy of the ΦPtH_x phase,

$$\begin{aligned}
 \ln G_2 &= \ln G_1(\eta_2) + N_{\Theta} \ln N_{\Theta} - N_H^{(\Theta)} \ln N_H^{(\Theta)} - (N_{\Theta} - N_H^{(\Theta)}) \ln(N_{\Theta} - N_H^{(\Theta)}) + \\
 &+ N_Q \ln N_Q - N_H^{(Q)} \ln N_H^{(Q)} - (N_Q - N_H^{(Q)}) \ln(N_Q - N_H^{(Q)})
 \end{aligned} \tag{21}$$

is thermodynamic probability of the ΦPtH_x phase, η_2 is the long-range order parameter in distribution of fullerenes over the sites of the ΦPtH_x phase.

The derived formula (19) shows the dependence of free energy f_2 of the ΦPtH_x phase on temperature T , concentrations c_1 , c_2 , c of Φ_1 , Φ_2 fullerenes and hydrogen, degree of ordering η_2 in this phase and energetic constants of pair interaction between Φ_n - Φ_m ($n, m=1, 2$) fullerenes, fullerenes and platinum atoms, fullerenes and hydrogen atoms. Below we shall study the free energy f_2 for hydrofulleride for the purpose of interpretation of calculation results.

6. Hydrofullerite ΦH_x . Free energy

The expression for free energy f_3 of this phase involves the terms of free energy f_1 of the ΦPt phase, depending on the energies of pair interaction between fullerenes Φ_n - Φ_m and their distribution over the lattice sites of the first and the second type, and the terms of free energy f_2 with energetic parameters of hydrogen atoms in positions Θ and Q .

The distribution of hydrogen atoms over all interstitial sites Θ , Q , D_1 , D_2 is taken into consideration. In the elementary cell we have eight Θ and eight Q interstitial sites as before, and also twenty four clastral D interstitial sites, eighteen of them are D_1 and six D_2 . These interstitial sites D_1 , D_2 have the nearest site at the distance of r' , clastral interstitial site D_1 has one nearest site of the first type, clastral interstitial site D_2 has one nearest site of the second type.

It should be mentioned that in the case when all interstitial sites Θ , Q , D_1 , D_2 are filled by hydrogen atoms, the ΦH_{10} hydrofullerite is formed with a maximum hydrogen content.

Considering formulae (8), (10), (12), the calculation of free energy f_3 for one lattice site for the ΦH_x hydrofullerite in dependence on temperature T , concentrations c_1 , c_2 , c of Φ_1 , Φ_2 fullerenes and hydrogen atoms, order parameter η_3 in this phase and energetic constants gives the following formula:

$$\begin{aligned} f_3 = \frac{F_3}{N} = & (E_3 - kT \ln G_3 - kT N_H \ln \lambda) / N = \\ & -6(c_1^2 \nu_{\Phi_1 \Phi_1} + c_2^2 \nu_{\Phi_2 \Phi_2} + 2c_1 c_2 \nu_{\Phi_1 \Phi_2}) - \frac{3}{8}(2\nu_{\Phi_1 \Phi_2} - \nu_{\Phi_1 \Phi_1} - \nu_{\Phi_2 \Phi_2}) \eta_3^2 + \\ & + \frac{1}{4} kT [3(c_1 + \frac{1}{4} \eta_3) \ln(c_1 + \frac{1}{4} \eta_3) + 3(c_2 - \frac{1}{4} \eta_3) \ln(c_2 - \frac{1}{4} \eta_3) + \\ & + (c_1 - \frac{3}{4} \eta_3) \ln(c_1 - \frac{3}{4} \eta_3) + (c_2 + \frac{3}{4} \eta_3) \ln(c_2 + \frac{3}{4} \eta_3)] - \\ & - c[20(c_1 \nu_{\Phi_1 H} + c_2 \nu_{\Phi_2 H}) + \frac{3}{2}(\nu_{\Phi_1 H} - \nu_{\Phi_2 H}) \eta_3] + \\ & + 10kT[c \ln c + (1-c) \ln(1-c)] - 10kT c \ln \lambda, \end{aligned} \quad (22)$$

where E_3 is configuration energy of hydrofullerite

$$\begin{aligned} E_3 = & -3N[P_{\Phi_1}^{(1)}(P_{\Phi_1}^{(1)} + P_{\Phi_1}^{(2)})\nu_{\Phi_1 \Phi_1} + P_{\Phi_2}^{(1)}(P_{\Phi_2}^{(1)} + P_{\Phi_2}^{(2)})\nu_{\Phi_2 \Phi_2} + \\ & + (2P_{\Phi_1}^{(1)}P_{\Phi_2}^{(1)} + P_{\Phi_1}^{(1)}P_{\Phi_2}^{(2)} + P_{\Phi_1}^{(2)}P_{\Phi_2}^{(1)})\nu_{\Phi_1 \Phi_2}] - \\ & - \frac{1}{2}(N_H^{(\Theta)} + N_H^{(Q)})[(6P_{\Phi_1}^{(1)} + P_{\Phi_1}^{(2)})\nu_{\Phi_1 H} + (6P_{\Phi_2}^{(1)} + P_{\Phi_2}^{(2)})\nu_{\Phi_2 H}] - \\ & - N_H^{(D_1)}(P_{\Phi_1}^{(1)}\nu_{\Phi_1 H} + P_{\Phi_2}^{(1)}\nu_{\Phi_2 H}) - N_H^{(D_2)}(P_{\Phi_1}^{(2)}\nu_{\Phi_1 H} + P_{\Phi_2}^{(2)}\nu_{\Phi_2 H}), \end{aligned} \quad (23)$$

$$\begin{aligned} \ln G_3 = & -\frac{1}{4}N(3P_{\Phi_1}^{(1)} \ln P_{\Phi_1}^{(1)} + 3P_{\Phi_2}^{(1)} \ln P_{\Phi_2}^{(1)} + P_{\Phi_1}^{(2)} \ln P_{\Phi_1}^{(2)} + P_{\Phi_2}^{(2)} \ln P_{\Phi_2}^{(2)} + \\ & + N_{D_1} \ln N_{D_1} - N_H^{(D_1)} \ln N_H^{(D_1)} - (N_{D_1} - N_H^{(D_1)}) \ln(N_{D_1} - N_H^{(D_1)}) + \\ & + N_{D_2} \ln N_{D_2} - N_H^{(D_2)} \ln N_H^{(D_2)} - (N_{D_2} - N_H^{(D_2)}) \ln(N_{D_2} - N_H^{(D_2)})) \end{aligned} \quad (24)$$

is thermodynamic probability of the ΦH_x phase. Below we shall fulfill the formula (22) study.

7. Pt crystal. Free energy of platinum

Free energy F_4 of platinum is calculated with regard to interaction between platinum atoms and for this crystal $G_4=1$, $\ln G_4=0$. So, in this case the calculation of free energy for platinum gives the following formula:

$$f_4 = F_4 / N = -6\nu_{pp}, \quad (25)$$

where ν_{pp} is energy of interaction between the nearest pairs of platinum atoms.

8. Discussion of theoretical results

Comparing equations (15), (19), (22), (25) for the free energies f_i ($i=1,2,3,4$) of all phases of chemical reaction (1), we can write these formulae as follows:

$$f_1 = -e_0 - e_1 - \omega_0 \eta^2 - \omega_1 \eta + \frac{1}{4} kT \Delta_{\eta}, \quad \text{for the } \Phi \text{Pt phase}, \quad (26)$$

$$f_2 = -e_0 - e_1 - \omega_0 \eta^2 - \omega_1 \eta - \omega_2 x \eta - \varepsilon_2 x + \frac{1}{4} kT \Delta_\eta + kT \Delta'_x - kTx \ln \lambda,$$

for the ΦPtH_x phase, (27)

$$f_3 = -e_0 - \omega_0 \eta^2 - \omega_3 x \eta - \varepsilon_3 x + \frac{1}{4} kT \Delta_\eta + kT \Delta''_x - kTx \ln \lambda,$$

for the ΦH_x phase, (28)

$$f_4 = -e_4, \quad \text{for the Pt phase,} \quad (29)$$

where the e_i and ω_i values for these phases are equal to, respectively:

$$\begin{aligned} e_0 &= 6(c_1^2 v_{\Phi_1 \Phi_1} + c_2^2 v_{\Phi_2 \Phi_2} + 2c_1 c_2 v_{\Phi_1 \Phi_2}), \\ e_1 &= 6(c_1 v_{\Phi_1 P} + c_2 v_{\Phi_2 P}), \\ \omega_0 &= \frac{3}{8}(2v_{\Phi_1 \Phi_2} - v_{\Phi_1 \Phi_1} - v_{\Phi_2 \Phi_2}), \\ \omega_1 &= v_{\Phi_1 P} - v_{\Phi_2 P}, \\ \omega_2 &= \frac{3}{40}(v_{\Phi_1 H} - v_{\Phi_2 H}), \quad \omega_3 = 2\omega_2, \\ \varepsilon_2 &= \frac{7}{4}(c_1 v_{\Phi_1 H} + c_2 v_{\Phi_2 H}), \quad \varepsilon_3 = \frac{8}{7}\varepsilon_2, \\ e_4 &= 6v_{PP} \end{aligned} \quad (30)$$

and

$$\Delta_\eta = 3(c_1 + \frac{1}{4}\eta) \ln(c_1 + \frac{1}{4}\eta) + 3(c_2 - \frac{1}{4}\eta) \ln(c_2 - \frac{1}{4}\eta) + \quad (31)$$

$$+ (c_1 - \frac{3}{4}\eta) \ln(c_1 - \frac{3}{4}\eta) + (c_2 + \frac{3}{4}\eta) \ln(c_2 + \frac{3}{4}\eta),$$

$$\Delta'_x = x \ln \frac{x}{4} + (4-x) \ln \frac{4-x}{4}, \quad (32)$$

$$\Delta''_x = x \ln \frac{x}{10} + (10-x) \ln \frac{10-x}{10}. \quad (33)$$

In the case of stoichiometric composition, when $c_1=3/4$, $c_2=1/4$, the energetic constants (30) take the forms:

$$\begin{aligned} e_0 &= \frac{3}{8}(9v_{\Phi_1 \Phi_1} + v_{\Phi_2 \Phi_2} + 6v_{\Phi_1 \Phi_2}), \\ e_1 &= \frac{3}{2}(3v_{\Phi_1 P} + v_{\Phi_2 P}), \\ \omega_0 &= \frac{3}{8}(2v_{\Phi_1 \Phi_2} - v_{\Phi_1 \Phi_1} - v_{\Phi_2 \Phi_2}), \\ \omega_1 &= v_{\Phi_1 P} - v_{\Phi_2 P}, \\ \omega_2 &= \frac{3}{40}(v_{\Phi_1 H} - v_{\Phi_2 H}), \\ \varepsilon_2 &= \frac{7}{16}(3v_{\Phi_1 H} + v_{\Phi_2 H}), \\ e_4 &= 6v_{PP}, \end{aligned} \quad (34)$$

and the Δ_η value will be equal to

$$\Delta_\eta = \frac{1}{4} \left[3(3+\eta) \ln \frac{3+\eta}{4} + 3(1-\eta) \ln \frac{1-\eta}{4} + 3(1-\eta) \ln \frac{3(1-\eta)}{4} + (1+3\eta) \ln \frac{1+3\eta}{4} \right]. \quad (35)$$

With these results in view of derived formulae (26)-(29) for free energies we can study the temperature dependence of hydrogen solubility in the ΦPtH_x , ΦH_x phases, define the equilibrium value of order parameter, investigate the phase transitions in considered system with increasing temperature, establish the conditions of their realization, evaluate the energetic constants of all components of chemical reaction (1), construct phase diagram of the system. Below we shall examine these problems.

9. The hydrogen solubility in ΦPtH_x , ΦH_x phases

The hydrogen solubility in each phase is defined by the equilibrium concentration of hydrogen atoms that can be found by minimization of free energies f_2 , f_3 with respect to concentration x of hydrogen atoms relative to the number of sites (fullerenes) of crystal lattice:

$$\partial f_2 / \partial x = 0 \text{ for } \Phi\text{PtH}_x \text{ phase and } \partial f_3 / \partial x = 0 \text{ for } \Phi\text{H}_x \text{ phase.} \quad (36)$$

Minimizing the expressions (27), (28), we find:

$$x = 4 \left[\frac{1}{\lambda} \exp \frac{-(\omega_2 \eta + \varepsilon_2)}{kT} + 1 \right]^{-1} \text{ for } \Phi\text{PtH}_x \text{ phase,} \quad (37)$$

$$x = 10 \left[\frac{1}{\lambda} \exp \frac{-(\omega_3 \eta + \varepsilon_3)}{kT} - 1 \right]^{-1} \text{ for } \Phi\text{H}_x \text{ phase.} \quad (38)$$

From these formulae it follows that:

$$x = \begin{cases} 0 & \text{at } T \rightarrow 0 \\ 4(1 + \frac{1}{\lambda})^{-1} & \text{at } T \rightarrow \infty \end{cases}, \text{ if } \omega_2 \eta + \varepsilon_2 < 0, \quad \left. \vphantom{x = \begin{cases} 0 \\ 4(1 + \frac{1}{\lambda})^{-1} \end{cases}} \right\} \text{ for } \Phi\text{PtH}_x \text{ phase,} \quad (39)$$

$$x = \begin{cases} 4 & \text{at } T \rightarrow 0 \\ 4(1 + \frac{1}{\lambda})^{-1} & \text{at } T \rightarrow \infty \end{cases}, \text{ if } \omega_2 \eta + \varepsilon_2 > 0,$$

$$x = \begin{cases} 0 & \text{at } T \rightarrow 0 \\ 10(1 + \frac{1}{\lambda})^{-1} & \text{at } T \rightarrow \infty \end{cases}, \text{ if } \omega_3 \eta + \varepsilon_3 < 0, \quad \left. \vphantom{x = \begin{cases} 0 \\ 10(1 + \frac{1}{\lambda})^{-1} \end{cases}} \right\} \text{ for } \Phi\text{H}_x \text{ phase.} \quad (40)$$

$$x = \begin{cases} 10 & \text{at } T \rightarrow 0 \\ 10(1 + \frac{1}{\lambda})^{-1} & \text{at } T \rightarrow \infty \end{cases}, \text{ if } \omega_3 \eta + \varepsilon_3 > 0.$$

At the sufficiently great activity of hydrogen atoms with increasing temperature in the ΦPtH_x phase the hydrogen solubility tends to the four ($x_0=4$) and in the ΦH_x phase it approaches the ten ($x_0=10$), i.e. with rise in temperature the respective ΦPtH_4 and ΦH_{10} phases with the maximum concentration of hydrogen will be formed.

Figure 2 illustrates the character of temperature dependence of hydrogen solubility in the ΦPtH_x and ΦH_x phases. The slope of this curve is determined by the numerical value of energetic constants, the order parameter value and the hydrogen atoms activity, which can be evaluated from independent experimental data. The knowledge of these values permits to evaluate numerically the hydrogen solubility at each temperature in the ΦPtH_x and ΦH_x phases and to estimate how it differ from the respective maximum value.

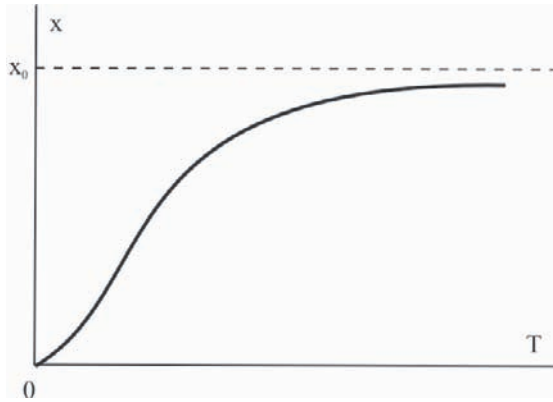


Figure 2. The character of temperature dependence of hydrogen solubility at the negative value of energetic parameter in exponent of formulae (37, 38). $x_0 = 4$ for the ΦPtH_x phase, $x_0 = 10$ for the ΦH_x phase.

10. Order in fullerenes distribution over lattice sites

The equilibrium value of order parameter can be found from the equilibrium condition:

$$\partial f_i / \partial \eta = 0, \quad i = 1, 2, 3. \quad (41)$$

After substitution of free energies (26)-(28) and (31) into (41) for the stoichiometric composition, when $c_1=3/4$, $c_2=1/4$, we get the equilibrium equation as follows:

$$\frac{kT}{\omega_0} = \frac{32}{3} (\eta + \delta) / \ln \frac{(1 + \frac{1}{3}\eta)(1 + 3\eta)}{(1 - \eta)^2}, \quad (42)$$

where

$$\delta = \begin{cases} \omega_1 / 2\omega_0 & \text{for } \Phi\text{Pt}, \\ (\omega_1 + \omega_2 x) / 2\omega_0 & \text{for } \Phi\text{PtH}_x, \\ \omega_3 x / 2\omega_0 & \text{for } \Phi\text{H}_x, \end{cases} \quad (43)$$

which defines the equilibrium value of the degree of long-range order depending on temperature.

The character of temperature dependence of order parameter $\eta = \eta(T)$ is defined to a large extent by the value and sign of the quantity δ . The evaluation showed that $\omega_1 > 0$, $\omega_2 < 0$, $\omega_3 = 2\omega_2 < 0$, as is shown later. It should be noted that energetic parameter ω_1 is defined by interaction between Φ -Pt pairs and energetic parameter ω_2 is determined by interaction between Φ -H pairs.

Setting the values for order parameter η over the interval $0 \leq \eta \leq 1$ in equation (42), we calculate temperature and subsequently construct the $\eta = \eta(T)$ plot. This dependence is given in Fig. 3 for values of δ (43) equal to $\pm 0,1; \dots; \pm 0,3$. Fig. 3 shows that at $\delta > 0$ the order is increased with increasing temperature compared to its value at $\delta = 0$, the $\eta(T)$ curve approximate asymptotically to the abscissa axis at $T \rightarrow \infty$. At $\delta < 0$ the order parameter is decreased at each value of temperature, the $\eta(T)$ curves pass below the curve at $\delta = 0$.

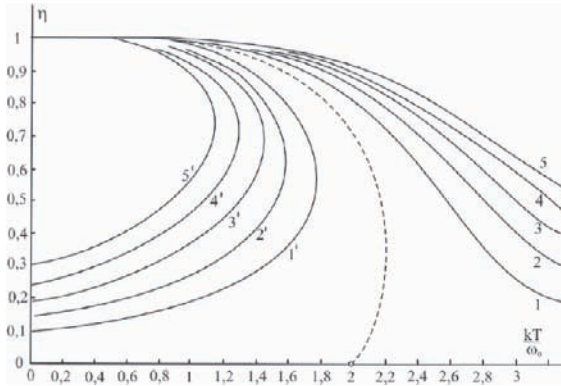


Figure 3. The curve plots of the temperature dependence of order parameter constructed by formula (42) for different values of energetic constant δ (43), equal to $\pm 0,1; \pm 0,15; \pm 0,2; \pm 0,25; \pm 0,3$ (curves 1-5 for $\delta > 0$ and curves 1'-5' for $\delta < 0$). The dotted line corresponds to $\delta = 0$, i.e. for pure fullerite without platinum and hydrogen atoms. The temperature T_c of loss of fullerite stable state (somewhat below the ordering temperature) is marked with circle on the abscissas axis.

Assuming in (41) $\delta = 0$, we can find the ordering temperature of pure fullerite. Considering formulae (26)-(28), we receive the equation of thermodynamically equilibrium state of fullerite of any composition as follows:

$$kT \ln \frac{(c_1 + \frac{1}{4}\eta)(c_2 + \frac{3}{4}\eta)}{(c_1 - \frac{3}{4}\eta)(c_2 - \frac{1}{4}\eta)} = \frac{32}{3} \omega_0 \eta. \quad (44)$$

Assuming $\eta \rightarrow 0$ in this equation, we define the composition dependence of temperature T_c of the loss of stable state of pure fullerite:

$$kT_c = \frac{32}{3} \omega_0 c_1 c_2. \quad (45)$$

In the case of stoichiometric composition $c_1=3/4$, $c_2=1/4$ the T_c temperature is equal to:

$$kT_c = 2\omega_0, \quad (46)$$

ω_0 is the ordering energy of pure fullerite.

Hence in the fullerite the order parameter value can be regulated varying its value to one or another side by the addition of metal impurity and also by hydrogenation. The order defines significantly the physical properties of fullerite.

11. Construction of constitution diagram

The evaluation of energetic constants of all components of the chemical reaction (1) has been performed with the use of experimental data on temperature ranges of phase transformations at different steps of the reaction. According to experimental data it is assumed that the formation of the ΦPtH_x hydrofulleride occurs at the temperature $T=475K$ and the ΦH_x hydrofullerite is formed at the temperature $T=650K$. Considering the values of order parameter by equations (42), (43), the following values for energetic parameters e_i and ordering energies ω_i in relation to ordering energy ω_0 of pure fullerite have been taken:

$$\begin{aligned} \omega_1 &= 1,9249; \quad \omega_2 = -1,5143; \quad e_2 = 1,3306; \\ e_0 &= 1,0160; \quad e_1 = -2,1912; \quad e_4 = -1,0560. \end{aligned} \quad (47)$$

According to the chosen values for energetic parameters (47) the plots of free energies in dependence on hydrogen concentration $f_i=f_i(c)$ have been constructed by formulae (26)-(29) over the region of ΦPtH_x and ΦH_x phases formation. The intersection points correspond to the points of phase transformations.

The phase diagram is given in Fig. 6. The full curves have been plotted by the intersection points of $f_i(c)$ curves and the dotted curves—with the use of the method of total tangent lines to them. Fig. 6 shows that at low temperatures the ΦPt (I) phase exists almost over all concentration range. The I→II phase transition to the ΦPtH_x phase (II) occurs with growing temperature, the transition temperature depends on hydrogen concentration and it rises with increasing concentration c , i.e. at low temperatures ($kT/\omega_0 \sim 0,035$) the hydride of fulleride of low-hydrogen content is formed. The hydrogen concentration is increased with a rise in temperature and we have $c \rightarrow 1$ at $kT/\omega_0 \sim 0,044$, i.e. all interstitial sites are occupied by hydrogen atoms. This corresponds to the increase of solubility with growing temperature. The ΦPtH_x phase (II) is realized over the wide range of temperature. At the rather high temperature ($kT/\omega_0 \sim 0,059$) the II→III phase transition takes place, the ΦH_x hydrofullerite is formed and the pure platinum is separated. The temperature of this phase transformation depends moderately on hydrogen concentration, it is found to be somewhat higher at low and great concentrations c . The $(\Phi H_x + Pt)$ phase (III) exists in the system over all concentration range beyond $kT/\omega_0 \sim 0,061$ temperature.

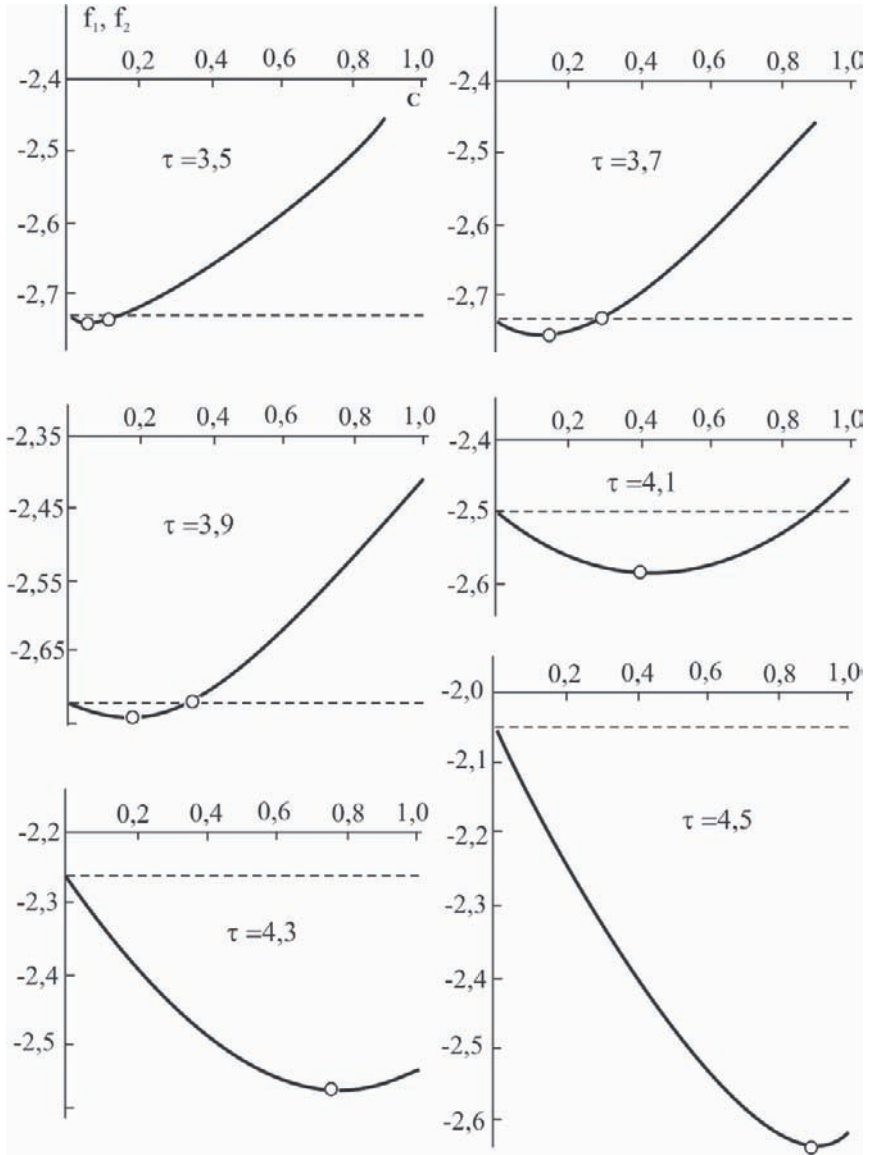


Figure 4. The curve plots of the concentration dependence of free energies f_1 (dotted lines) and f_2 (full curves) in the region of temperatures of phase transitions I $\rightarrow$ II ($\Phi\text{Pt} \rightarrow \Phi\text{PtH}_x$). The intersection and extremal points are marked with circles. $\tau = kT \cdot 10^2 / \omega_0$.

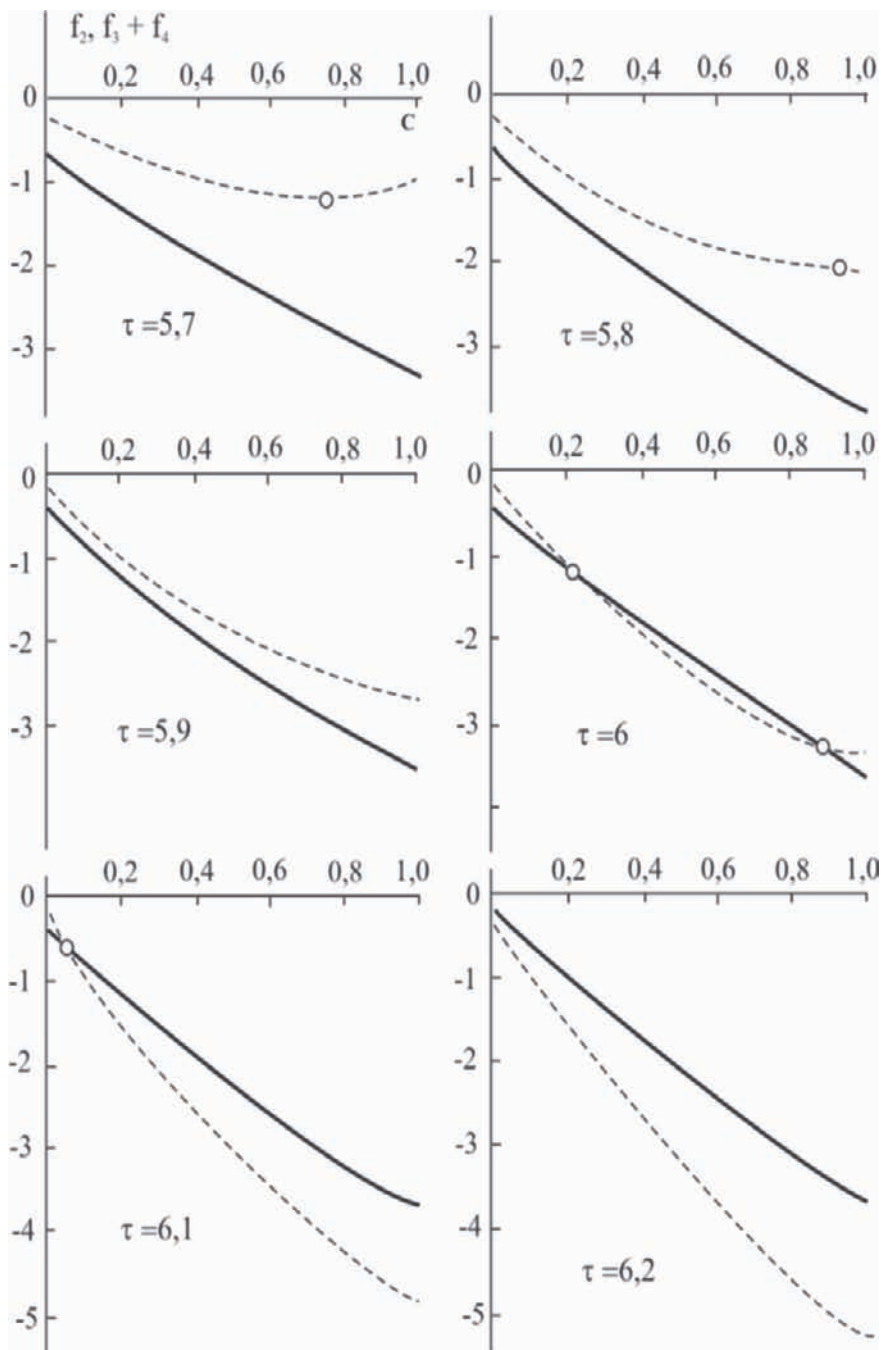


Figure 5. The curve plots of the concentration dependence of free energies f_2 (full curves) and f_3+f_4 (dotted curves) in the region of temperatures of phase transitions II $\rightarrow$ III ($\Phi\text{PtH}_x \rightarrow \Phi\text{H}_x + \text{Pt}$). The intersection and extremal points are marked with circles. $\tau = kT \cdot 10^2 / \omega_0$.

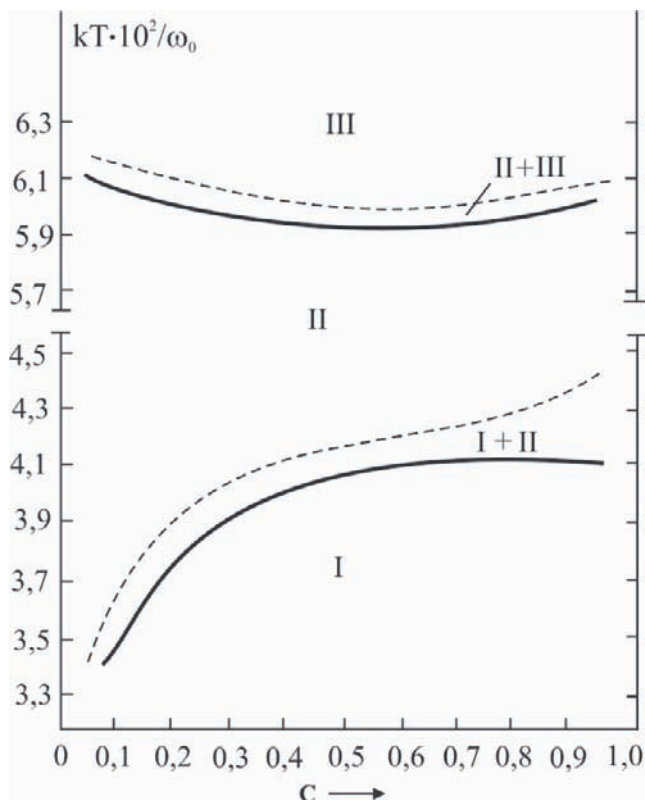


Figure 6. The phase constitution diagram of chemical reaction (1). The areas between full and dotted curves correspond to the two-phase state of system. Designations: I- ΦPt , II- ΦPtH_x , III- ΦH_x .

12. Conclusions

The elaborate statistical theory of phase transformations of chemical reaction (1) makes possible the explanation and substantiation of formation of phases of fulleride hydrides and then of fullerite with increase in temperature. The calculation of phases free energies has been performed using the rough simplified assumptions. The dependence of free energies of phases on their composition, temperature, order parameter in fullerenes subsystem, energetic constants has been found. The evaluation of energetic constants has been carried out with the use of experimental data for concentration and temperature ranges of each phase realization.

The temperature dependence of hydrogen solubility in ΦPtH_x and ΦH_x phases has been defined. As is shown in paper, with increasing temperature the hydrogen content in phases rises and approaches the state of full filling of all interstitial sites by hydrogen atoms.

The temperature and concentration dependence of order parameter in ΦPt , ΦPtH_x , ΦH_x phases has been studied. It has been shown in what cases with a rise in

temperature the order parameter decreases or increases up to ∞ depending on the chemical nature of impurity (hydrogen or platinum) and hydrogen concentration.

The energetic parameters of components of chemical reaction (1) have been evaluated. The curves of concentration dependence of phases free energies have been plotted for different temperatures. From these curves it is evident the increase of equilibrium concentration of hydrogen in ΦPtH_x and ΦH_x phases with increasing temperature.

An analysis of the curves of concentration and temperature dependences of free energies provides a possibility of phase diagram construction and this diagram defines the concentration and temperature regions of all phases realization. The phase diagram corresponds to experimental data of manifestation of phases of chemical reaction (1) in the course of temperature rise.

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INVESTIGATION OF MECHANISM OF FULLERENE DISSOLUTION IN AROMATICAL HYDROCARBONS

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Abstract. A comparative investigation of C_{60} fullerene solubility and donor force of alkyl derivatives of benzene has been performed. Based on the found correlation, which was determined by current methods, between C_{60} solubility and donor force of solvents, it has been concluded that the process of C_{60} dissolution in aromatic hydrocarbons is a process of intermolecular interaction combined with charge-transfer and formation of complexes of the donor-acceptor type. The agreement between a series of physical and chemical phenomena (factors, properties) observed in studies of C_{60} solubility and a number of existing criteria which allow the phenomena to be interpreted as a manifestation of the charge-transfer interaction substantiates our conclusion.

Keywords: fullerene, solubility, π -complex, electrophilic substitution, aromatic hydrocarbons.

1. Introduction

An appreciable C_{60} fullerene solubility is observed in many solvents relating to different classes of organic compounds as evidenced by experimental results. The process of C_{60} dissolution in solvents of different chemical nature is mainly interpreted in the context of an old based on experience rule "the similar dissolves in the similar". Different physical and chemical properties of substances are considered as the similarity factor.

Based on a study of C_{60} fullerene solubility [1], it has been found that C_{60} fullerene, being a nonpolar molecule, is insoluble in polar solvents, such as alcohol, acetone, tetrahydrofuran etc. Relying on the above, it has been concluded that the solvation mechanism of dissolving plays an insignificant part in the processes of fullerene dissolution.

Low solubility of C_{60} fullerene is observed in alkanes. As noted in [2], C_{60} solubility is somewhat improved with increasing number of carbon atoms in a chain.

The analysis performed in [3] has revealed that fullerenes dissolve best in the solvents for which specific enthalpy of evaporation referring to the specific volume of a solvent molecule is close to that for fullerene.

As noted in [2], fullerenes dissolve better in aromatic hydrocarbons and their derivatives, among which naphthalene derivatives occupy the first place. High

fullerene solubility in aromatic compounds is also interpreted in the context of an empirical rule "the similar dissolves in the similar". It is well known that one or several benzene rings form a basis for aromatic compounds. The rings have a structure much like regular hexagons which form a fullerene surface. From the above reasoning it is suggested that high fullerene solubility in aromatic solvents is due to magnetic interaction of the ring current which flows in a solvent molecule and the respective current in a fullerene molecule. Magnetic field, which was caused by the intramolecular ring current in a six-membered fullerene ring, orients a molecule of an aromatic compound so that the current inside this molecule is directed towards the current of a fullerene ring. This initiates the dissolution process [2].

When considering findings on C_{60} fullerene solubility in more detail, we have found that the rule "the similar dissolves in the similar" is not often obeyed. This is illustrated by the data given in Table 1.

TABLE 1. Dipole moments of solvents and C_{60} fullerene solubility

Solvent	Dipole moment	Solubility, mg·ml ⁻¹
Pyridine	2,20	0,89 [3]
Benzene	0	1,50 [35]
Paraxylene	0	5,90 [35]
Metaxylene	0,37	1,40 [35]
Orthoxylene	0,62	8,70 [35]
Bromobenzene	1,57	2,80 [35]
CS ₂	0	7,90 [3]

As the table indicates, C_{60} fullerene solubility is practically the same in nonpolar benzene and polar pyridine. Like benzene, pyridine has a pronounced "aromatic" nature, i.e. electron distribution in a pyridine molecule is identical to that in benzene. However pyridine has a reasonable dipole moment as opposed to benzene.

C_{60} solubility in paraxylene is approximately four times greater than in benzene with both of these solvents are nonpolar and rated in the aromatic compound class.

The increase in dipole moments is observed in a sequence of aromatic compounds: paraxylene, metaxylene, orthoxylene, bromobenzene. However the correlation between the magnitudes of dipole moments of solvents and the magnitudes of C_{60} solubility in these solvents is not observed (Table 1).

Relatively high C_{60} solubility in carbon disulfide attracts particular interest (without comments). Carbon disulfide has no dipole moment and is sometimes assigned to the derivatives of aliphatic methane.

Experimental results given in Table 1 are only a small part of the available data. They suggest that C_{60} fullerene solubility in different classes of organic compounds is a complicated process.

2. The main types of intermolecular interactions

According to current concepts of the theory of solutions, the magnitude of any compound solubility results from interacting force between compound molecules and solvent molecules. A quantitative expression for the force of intermolecular

interaction is an interaction potential. The interaction potential is obtained experimentally and calculated using a body of mathematics of quantum theory [4-8].

Theoretical consideration reveals that intermolecular interactions have mainly an electrostatic nature. Energy of interactions depends on the electron density distribution of reacting molecules.

The following main contributions to the combined interaction between molecules may be approximately distinguished:

1. exchange interaction which appears due to an appreciable overlap of occupied electron shells in molecules and diminishes quickly with increasing intermolecular distance (U_{ex});
2. direct electrostatic interaction results from constant electric moments - dipole, quadrupole etc. which both of interacting molecules have. This is related to that the charge distribution on an isolated molecule is not spherically symmetric (U_{el});
3. induction (polarization) interaction is related to the electron density redistribution of one molecule in the field of another molecule having a constant electric moment (U_{ind});
4. dispersion interaction is due to correlation in instantly distributed electron densities of molecules. The dispersion interaction appears between any molecules including those not having constant electric moments (U_{disp});
5. interaction caused by the charge transfer, i.e. the electron density redistribution between interacting molecules (U_{red}).

Depending on the nature of interacting molecules, some interactions may be negligible or equal to zero. Direct electrostatic, induction and dispersion interactions are combined in a general concept of van der Waals nonspecific interactions which are not related to the electron shell overlap.

The process of electron density redistribution during charge-transfer interaction is accompanied by the more significant decrease in the system energy than in the case of van der Waals interactions. This suggests that the bond in the forming systems is stronger.

Charge-transfer interaction appears only in the case when one of the reacting molecule is an electron acceptor and the other one is an electron donor. Formation of charge-transfer complexes is a consequence of such interactions.

3. Objective of the work

C_{60} and C_{70} fullerenes are good electron acceptors [9, 10]. They are reduced readily and reversibly in the basis and excited states [11-15].

Owing to their electron-seeking properties, fullerenes form charge-transfer complexes with the substances capable for donating their electrons [16-19].

A large body of experimental research in different countries has revealed that aromatic hydrocarbons with extensively studied electron-donor capacity are the best solvents for C_{60} fullerene [6, 20].

Hence C_{60} fullerene molecules in aromatic solvents can a priori enter into intermolecular charge-transfer interactions with aromatic hydrocarbon molecules to form complexes of the donor-acceptor type.

In relation to the above, the objective of the work was to investigate correlation between electron-donor properties of solvents and C_{60} solubility.

4. Donor-acceptor interactions

At present much research is devoted to donor-acceptor interactions [6, 20-22]. Donor-acceptor properties of solvents are also investigated [21, 23].

Molecules must be ionized easily in order to be electron donors. There exist two such cases: π -electrons in conjugate electron systems (alkenes, alkynes and aromatic

hydrocarbons) and p -electrons in the substances which molecules contain heteroatoms with an unshared electron pair, such as alcohols, organic sulfides, iodides and nitrous bases in which unshared pairs are localized at the atomic orbitals of oxygen, sulfur, iodine and nitrogen, respectively.

Research on charge-transfer complexes has revealed that they can be divided into many types. Molecular complexes are typically considered by the nature of orbitals at which the electrons participating in the charge transfer are situated. In the unsaturated systems π -electrons can be transferred to the σ -orbitals or in the π -systems of acceptor molecules. This gives rise to complexes of π - σ - and π - π -types.

Aromatic hydrocarbons which contain heteroatoms, such as nitrogen, sulfur, oxygen and act as p -donors can form complexes of π - π -, π - σ - and p - π -types.

5. Polarization of the electron system of an aromatic core

Benzene, the classical progenitor of aromatic compounds, has six p -electrons for which one can envision an infinite conjugation along the closed ring. Particular "aromatic" properties of this system has been explained on the basis of quantum-mechanical concepts. According to these concepts, all six p -functions are overlapped. This leads to uniform distribution of an electron π -cloud along the benzene ring, and therefore all carbon atoms in benzene are equivalent. This concept has found experimental verification by the fact that substitution of one carbon atom in the benzene ring for the other one or a group of atoms always gives rise to the only one isomer.

Substitution of two hydrogen atoms gives rise to three isomers: *ortho*-, *meta*- and *para*-. If each carbon atom in all positions in the mono-substituted aromatic ring had equal electron density, a quantitative ratio of the isomers would be as follows: 40% *ortho*-, 40% *meta*-, 20% *para*-isomers. However experimental data reveal that this is not the case. Substitution of one hydrogen atoms for the other one or a group of atoms brings about the redistribution in electron density of the benzene core in consequence of polarizing effect of a substituent. The resulting electrostatic field affects not only σ -electrons, but also π -bonds and unshared pairs of the p -type. The weaker π -bond is much more susceptible to the polarizing effect than the stronger σ -bond. When considering polarization, σ -bonds demonstrate the induction effect of a substituent, and no other. Polarization of a π -bond and a p -electron cloud in the conjugate systems are reckoned among the mesomerism phenomena which research is related to the mesomeric effect of a substituent.

Each induction and mesomeric effect is assigned positive or negative importance. Their influences can be superimposed in the same or opposite directions.

There exist two groups of substituents: electron-donor and electron-seeking. $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, and $-\text{CH}_3$ etc. fall in the first group. These substituents are assigned a positive mesomeric effect (+M) (Fig. 1a).

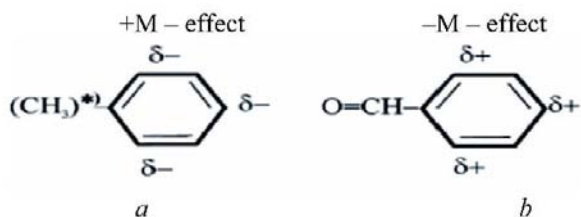


Figure 1. Effect of substituents on electron density distribution: *a* – positive mesomeric effect; *b* – negative mesomeric effect.

* Alkyl groups are substituents with a positive induction effect which increases electron density in a series: *ortho*- > *meta* > *para*-positions. The secondary effect of conjugation imparts an additional negative charge in the *ortho*- and *para*-positions. The resulting action of both of these effects is similar to that of a positive mesomeric effect.

Being electron donors, they donate *p*-electrons to the benzene core what causes π -electron density in the *ortho*- and *para*-positions in the benzene core to increase. $-\text{NO}_2$, $-\text{CN}$, $-\text{CHO}$ etc. fall in the second group. These substituents have a negative mesomeric effect ($-M$) (Fig. 1b) and draw off π -electrons from the benzene core with the result that carbon atoms in the *ortho*- and *para*-positions become positively charged and electron density is localized at carbon atoms in the *meta*-positions.

Inductive and mesomeric effects are responsible for electron distribution in a molecule unaffected by external influence. According to the electron affinity for a partner, positions with high or low electron density can serve as reaction centers.

Substituents which act inductively ($\pm I$) change σ -electron density in all positions in an aromatic core. This influence decreases in a series *ortho*-, *meta*-, *para*- because the inductive effect is distance dependent.

Influence of $\pm M$ -effect on π -electron distribution can appear only in the *ortho*- and *para*-positions rather than in the *meta*-positions.

6. Electron-donor activity of alkyl-benzenes

Donor activity of alkyl-benzenes which participate in the processes of intermolecular charge-transfer interactions has been much investigated by current methods [20-22].

Binding energies of complexes, equilibrium constants, spectral band shift in complexing etc. have been determined.

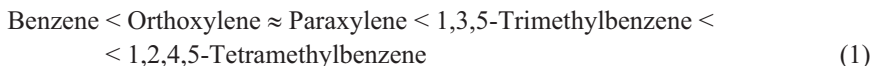
Mobile π -electrons in the benzene ring can be transferred to the σ -orbitals or in the π -systems of acceptor molecules what gives rise to π - σ - or π - π -complexes.

In the first case there appear complexes of the $\text{MX}_3 \cdot \text{Ar}$ type where $\text{M} = \text{Al}$, As , Sb etc., $\text{X} = \text{Br}$, Cl , and Ar – an aromatic molecule, such as benzene the benzene substituted.

Such complexes have been studied by the method of nuclear quadrupole resonance (NQR) in a number of work [24-28].

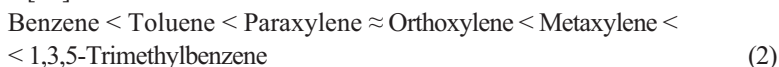
There exist complexes of benzenes with bromine [29] and halogen methanes CHCl_3 , CCl_4 [30-33]. Large number of complexes of the π - π -type are known [33].

Based on the results obtained by the NQR method it has been found that donor activity of an aromatic molecule depends upon the number of methyl substituents added to benzene. A series of increasing donor force have been obtained in [28]:



Similar results have been obtained [23] in determining spectroscopic equilibrium constants and enthalpy of complexing 1,3,5-trinitrobenzene (as an acceptor) with aromatic hydrocarbons (as electron donors). Based on the results, it has been also inferred that donor force of alkyl-benzenes increases with increasing number of methyl substituents.

A series of methyl derivatives of benzene has been studied by the method of spectral analysis in the UV region. The position of an absorption band for π - σ -complexes of alkyl-benzenes with iodine as an electron acceptor has been determined. A series of increase of donor force of benzene methyl derivatives have been derived [34]



These findings have revealed that donor force of methyl derivatives increases with increasing number of methyl substituents.

However these evaluations are conventional to a certain extent because characteristics of donor-acceptor interactions are affected by many factors, and the consequence of donor properties in a series of molecules is variable according to which acceptor is taken to evaluate these properties.

7. C_{60} fullerene solubility in benzene derivatives

7.1. METHYL DERIVATIVES OF BENZENE

Analysis of the data on C_{60} fullerene solubility in methyl derivatives of benzene has revealed that this magnitude depends not only on the number of CH_3 -groups, but also on their position in the benzene core. Fig. 2-6 show the structural formulae for methyl derivatives of benzene, the positions of methyl groups and the magnitudes of C_{60} solubility [1].

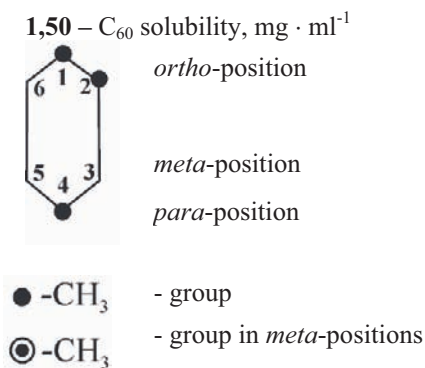


Figure 2. Benzene ring, positions of symbols and magnitudes of C_{60} fullerene solubility.

As illustrated in Fig. 3 *c,e*, the increase in C_{60} solubility in benzenes with two substituting $-CH_3$ groups is observed only in ortho- and paraxylenes. In metaxylene the magnitude of C_{60} solubility is identical to that in benzene (Fig. 3 *a*).

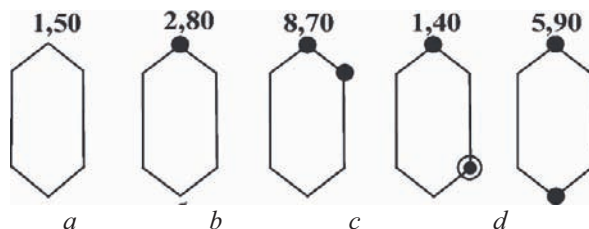


Figure 3. Dependence of C_{60} solubility on the positions of two CH_3 -groups in the benzene core.

Figures 4 *a, b, c* illustrate the position effect of three CH_3 -groups on C_{60} solubility. C_{60} solubility increases compared to that in orthoxylene (Fig. 4 *a*) if the third $-CH_3$ group is located in the *para*-position (Fig. 4 *a, c*) and decreases if this group is located in the *meta*-position (Fig. 4 *a, b*). If both of these methyl groups are in the *meta*-positions, their presence does not change dissolving ability of benzene. C_{60} solubility in 1,3,5-trimethylbenzene is identical to that in benzene (Fig. 5 *a, c*).

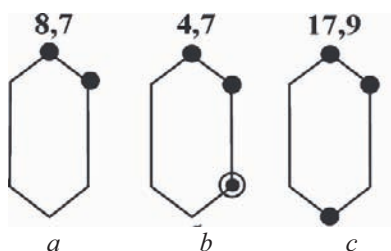


Figure 4. Dependence of C_{60} solubility on the positions of three CH_3 -groups in the benzene core.

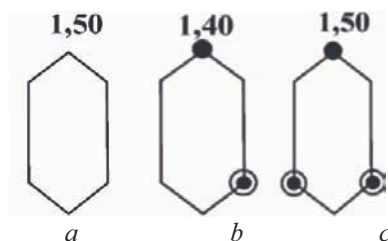


Figure 5. C_{60} solubility is invariant under effect of the methyl groups located in the *meta*-positions of the benzene core.

Summing the presented data, one can write the following series (3) of methyl derivatives of benzene in which C_{60} fullerene solubility increases (Fig. 6):

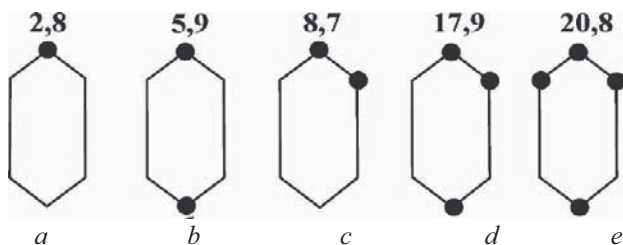


Figure 6. Series of increasing C_{60} solubility in methyl derivatives of benzene.



Donor activity of these compounds changes in the same sequence as shown above (series 1, 2) excluding methyl derivatives with CH_3 groups located in the *meta*-positions. These groups drop out of this series.

Parallelism found in the present work between increasing donor activity and dissolving power of methyl derivatives of benzene confirms the assumption of existing charge-transfer interaction between C_{60} molecules and molecules of methyl derivatives of benzene.

The increase in C_{60} solubility in methyl derivatives of benzene with increasing number of methyl groups in the benzene core is regular. Having electron donor properties, each methyl group increases the total π -electron density of the benzene core. A negative charge is largely localized in the *ortho*- and *para*-positions under the action of a positive mesomeric effect of the CH_3 group.

This also suggests that reaction centers for interaction between C_{60} molecules with π -electron density of the benzene core are carbon atoms located in the *ortho*- and *para*-positions. In this case the *ortho*-position is more preferential because C_{60} solubility increases two times if a subsequent CH_3 -group occupies the *para*-position and three times if this group occupies the *ortho*-position. It can be seen in comparing Fig. 6 *a* with Fig. 6 *b*; Fig. 6 *c* with Fig. 6 *d*; Fig. 6 *a* with Fig. 6 *c*.

Typically, electron density of different carbon atoms in the benzene core is judged from the amount of isomers (%) which form on electrophilic substitution of hydrogen in the benzene core for an electrophilic group, such as nitroxyl in the mononitration.

It is agreed that attack of an electrophilic reagent is directed towards the most reactive centers of a core with high electron density. These centers are carbon atoms in the *ortho*- and *para*-positions of the benzene substituted if a substituting group is an electron donor, and in the *meta*-positions if a substituting group is an electron acceptor.

In further discussion of C_{60} fullerene solubility in benzene derivatives we will compare its magnitude with quantitative distribution of nitro isomers which form in the reactions of electrophilic substitution of the benzene derivative considered.

7.2. ALKYL DERIVATIVES OF BENZENE

C_{60} solubility in alkyl-benzenes decreases in a series:



Activating action of substituting groups, from the methyl one to the tertiary-butyl one, decreases in the similar order in the electrophilic substitution reactions. This is illustrated by decreasing total amount of *ortho*- and *para*-isomers (Table 2).

Experimental results on amounts (%) of isomers which form in the alkyl-benzenes mononitration, and C_{60} solubility in alkyl-benzenes are given in Table 2.

TABLE 2. Isomer ratio (%) in the nitration of alkyl-benzenes and C_{60} fullerene solubility in alkyl-benzenes [34]

Alkyl-benzene	Isomers ratio %			C_{60} solubility mg·ml ⁻¹
	<i>ortho</i> -	<i>meta</i> -	<i>para</i> -	
Toluene	58,5	4,4	37,1	2,90 [35]
Ethyl benzene	45,0	6,5	48,5	2,16 [37]
Isopropyl benzene	30,0	7,7	62,3	1,20 [35]
Tert-butyl benzene	15,8	11,5	72,7	0,90 [35]

As the table indicates C_{60} solubility and the amount of *ortho*- nitro isomers increases concurrently, i.e. with increasing π -electron density in the *ortho*-positions of alkyl derivatives of benzene.

Experimental results given in Table 2 are presented graphically in Fig. 7 in the coordinates " C_{60} solubility (mg·ml⁻¹)/amount of respective isomer (%)".

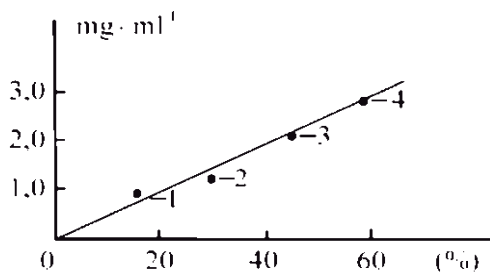


Figure 7. C_{60} fullerene solubility (mg·ml⁻¹) in 1 – tert-butyl benzene; 2 – isopropyl benzene; 3 – ethyl benzene; 4 – toluene, as a function of the amount of respective *ortho*-isomer (%) (= of the π -electron density in the *ortho*-position).

The plot is a straight line passing through the origin of the coordinates. This is evidence that C_{60} solubility depends linearly on the π -electron density in the *ortho*-position of alkyl derivatives of benzene.

7.3. HALOGEN DERIVATIVES OF BENZENE

Substituting halogens are assigned a positive mesomeric and a negative induction effects. C_{60} solubility in halogen derivatives of benzene increases in a series:



At first glance when considering haloids electronegativity, C_{60} solubility in iodobenzene should be higher than in chlorobenzene because ability of the substituent to give its unshared electron pair to form a double bond is inversely proportional its electronegativity. In this case one should expect the +M effect to be increased in a series of substituents:



In this connection C_{60} solubility in the benzene halogenated should be also increased in the same sequence.

In reality this is not the case. A fluorine atom is the best electron donor in a series of halogens. This is attributed to that the delivered unshared p -electron pair of the haloid is located at the $2p$ -electron shell only in a fluorine atom while chlorine ($3p$), bromine ($4p$) and iodine ($5p$) shells are less favorable by their size for overlapping with the $2p$ -electron shell of carbon.

C_{60} solubility increases in the similar sequence, from iodobenzene to chlorobenzene. The exception is fluorobenzene in which C_{60} solubility is lower than in iodobenzene. Apparently, in the case of interaction between fluorobenzene and C_{60} fullerene the factor of high fluorine electronegativity prevails. Moreover, as Table 3 indicates the fluorobenzene nitration gives rise to mainly *para*-isomer and very little *ortho*-isomers. Consequently, the entire negative charge is localized in the *para*-position in a fluorobenzene molecule. Therefore, as with C_{60} solubility in alkyl derivatives of benzene (Table 2), one can anticipate that for the C_{60} molecule that is an electrophilic reagent, the *ortho*-position will be the more preferential location for electrophilic attack than the *para*-position.

As with substituting methyl groups, C_{60} solubility increases with increasing number of substituting haloid atoms to two atoms if they are in the *ortho*-positions. C_{60} solubility decreases if these atoms are in the *meta*-positions.

TABLE 3. Isomer ratio (%) in the mononitration of halogen derivatives of benzene and C_{60} fullerene solubility in these derivatives [34]

Available substituent	Ratio of resulting isomers, %			C_{60} solubility, mg·ml ⁻¹	
Electron donor substituents	<i>ortho</i> -	<i>meta</i> -	<i>para</i> -		
-F fluorobenzene	12,4	–	87,6	1,20	[35]
-Cl chlorobenzene	29,6	0,9	69,5	5,70	[35]
-Br bromobenzene	36,5	1,2	62,3	2,80	[35]
-I iodobenzene	37,9	2,1	60,0	2,10	[35]

TABLE 4. C₆₀ fullerene solubility in halogen derivatives of benzene

Halogen derivatives of benzene	C ₆₀ solubility, mg·ml ⁻¹
Chlorobenzene	5,70 [35]
<i>Ortho</i> -dichlorobenzene	24,6 [35]
<i>Meta</i> -dichlorobenzene	2,40 [35]
<i>Ortho-para</i> -trichlorobenzene	10,40 [35]
Bromobenzene	2,80 [35]
<i>Ortho</i> -dibromobenzene	13,80 [35]
<i>Meta</i> -dibromobenzene	13,80 [35]

Further increase in the number of chlorine atoms tends to decrease C₆₀ solubility even if these atoms are in the *ortho*- and *para*-positions.

C₆₀ solubility in *ortho-para*-trichlorobenzene (10,40 mg·ml⁻¹) is 2.5 times less than it is in *ortho*-dichlorobenzene (24.6 mg·ml⁻¹) (Table 4).

7.4. BENZENE DERIVATIVES WITH ELECTRON-SEEKING SUBSTITUTING GROUPS

–NO₂, –C≡N, –CHO groups are strong electron acceptors which delocalize a negative charge of the benzene core. The benzene core acquires a partial positive charge localized in the *ortho*- and *para*-positions as a result of the negative inductive and particularly the negative mesomeric effects of aromatic compounds. The negative charge is localized principally in the *meta*-positions. As evident from the data given in Table 5, C₆₀ solubility in nitrobenzene, benzaldehyde, benzonitrile is very low.

 TABLE 5. Isomer ratio (%) in the mononitration of benzene derivatives and C₆₀ fullerene solubility in these derivatives [34]

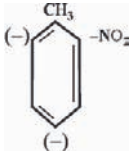
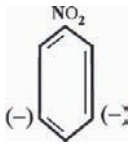
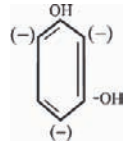
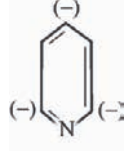
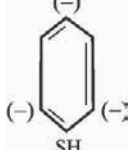
Available substituent	Ratio of resulting isomers, %			C ₆₀ solubility, mg·ml ⁻¹
	<i>ortho</i> -	<i>meta</i> -	<i>para</i> -	
Electron-seeking substituents				
–NO ₂ nitrobenzene	6,4	93,3	0,3	0,80 [3]
–CHO benzaldehyde	19,0	72	9,0	0,42 [37]
–CN benzonitrile	17	81	2,0	0,41 [3]

These findings especially clearly stress dependence of C₆₀ dissolution on the electron density in the *ortho*- and *para*-positions in the benzene core and indifference of this process to the electron density in the *meta*-positions.

The magnitudes of C_{60} solubility in nitrobenzene and *ortho*-nitrotoluene are a further example of dependence of C_{60} solubility only on the π -electron density in the *ortho*- and *para*-positions and its indifference to the negative charge localized in the *meta*-positions. For nitrobenzene, the negative charge is localized principally in the *meta*-position (Table 5) and in this case C_{60} solubility is rather low, 0.80 mg·ml⁻¹.

For *ortho*-nitrotoluene, the negative charge is localized largely in the *ortho*- and *para*-positions (mononitration of *ortho*-nitrotoluene gives rise only to 2,6- and 2,4-dinitrotoluenes) and C_{60} solubility in this solvent is three times greater than that in nitrobenzene (Tables 5 and 6).

TABLE 6. Isomer distribution in the mononitration of aromatic solvents and magnitudes of C_{60} solubility in these solvents

Solvent		Isomer distribution, %			C_{60} fullerene solubility, mg·ml ⁻¹
Name	Structural formula	Ortho-	Meta-	Para-	
2-nitrotoluene		+	–	+*)	2,45 [37]
Nitrobenzene		6,4	93	0,4	0,80 [3]
Methoxybenzene (Resorcin)		+	little	+	5,60 [3]
Pyridine		+	?	+	0,89 [3]
Thiophenol		+		+	6,91 [38]

*) (+) – isomer forms,
(–) – isomer does not form.

7.5. RESORCIN (METHOXYBENZENE)

A methoxybenzene molecule contains two OH-groups with strong positive mesomeric effect.

Mutual influence of two OH-groups ensures the easy entry of resorcin into the reactions of electrophilic substitution mainly in the *para*- and *ortho*-positions. Consequently, π -electron density of resorcin is localized in the *ortho*- and *para*-positions what makes C_{60} solubility relatively high, $5.60 \text{ mg}\cdot\text{ml}^{-1}$ (Table 6).

7.6. PYRIDINE

C_{60} solubility in pyridine is identical to that in benzene. Pyridine has a pronounced "aromatic" nature. π -electron distribution in a pyridine molecule is identical to that in benzene. Pyridine has six mobile π -bonds, one of them is formed by an unshared pair of *p*-electrons of a nitrogen atom. Pyridine can be nitrated. A nitro group enters the β -position. Because carbon with the highest electron density is a center for electrophilic substitution, one can make a logical assumption that the reaction center for charge-transfer interaction between pyridine molecules and C_{60} is also in the β -position or, what is equivalent, in the *ortho*-position relative to a nitrogen atom (Table 6).

7.7. THIOPHENOL

Thiophenol is an aromatic compound (Table 6). One hydrogen atom in its benzene core is substituted for a SH-group. The SH-group has a weak negative induction and a positive mesomeric effects. In addition, the unshared pair of *p*-electrons of a sulfur atom contributes to the π -electron cloud of the benzene ring.

C_{60} solubility in thiophenol is more than 2 times greater than that in toluene as opposed to pyridine. Improved C_{60} solubility in thiophenol is attributable to the increase in the overall π -electron density of the benzene core. When acted upon by a positive mesomeric effect of a SH-group, π -electron density is localized mainly in the *ortho*- and *para*-positions, i.e. in the reaction centers for interaction between thiophenol molecules and C_{60} .

8. Discussion of results

The revealed correlation between donor activity of methyl derivatives of benzene and C_{60} solubility in these derivatives allows a consideration of the C_{60} dissolution process as a process of intermolecular charge-transfer interaction.

In addition, there exist other factors revealed by studies on C_{60} fullerene solubility. These factors conform to the requirements of a number of criteria, which were formulated on a basis of studies of charge-transfer processes, and enable identification of the charge transfer:

- charge-transfer interaction occurs between the molecules one of them is an electron donor and the other one is an electron acceptor;
- interaction must be reversible;
- interaction may be defined by the presence of an absorption band. It is thought that the charge-transfer band is at 300 nm in the UV range [22].

As may be seen from the data given in the present work, it has been justified theoretically and confirmed experimentally that aromatic hydrocarbons are electron donors and C_{60} molecules are electron acceptors and in this connection they can form charge-transfer complexes.

When studying absorption spectra of C_{60} in toluene solutions [39], we have found that with increasing C_{60} concentration there appears a bathochromic shift of the absorption band for C_{60} fullerene with a maximum at $\lambda = 335$ nm. According to the literature data, absorption in this region may be defined as a charge-transfer band.

C_{60} dissolution in aromatic hydrocarbons is equilibrium. Only C_{60} crystals form in the solvent evaporation.

Bright color of C_{60} solutions also indicates that charge-transfer complexes exist in these solutions in aromatic hydrocarbons.

All the factors confirm the made conclusion on the mechanism of C_{60} dissolution.

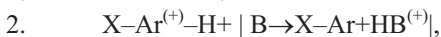
The examples of C_{60} dissolution in benzene derivatives considered in the present work evidence the clear dependence of C_{60} solubility on the electron density distribution in the benzene ring. We have identified a priori the electron density with the distribution of *ortho*-, *meta*-, *para*-isomers which form in the reactions of electrophilic substitution of the benzene derivative considered. This identification is evaluated but in some cases, such as in a series of homologs for alkyl derivatives of benzene, the total agreement between the C_{60} solubility and the amount of *ortho*-isomers is observed (Table 2 and Fig. 7).

The parallels observed between C_{60} solubility and electrophilic substitution products are regular if C_{60} dissolution in aromatic hydrocarbons is considered as acid-base relationships. According to the theoretical research and experimental results, double bonds of aromatic hydrocarbons with mobile π -electrons are Lewis base. Consequently, they react with acids and Lewis acids to form complexes. It has been established that these complexes cannot be to a marked extent electrostatic. It has been found that they are often colored. Complexes with iodine (Lewis acid) give absorption bands at 300 nm in the UV region. These complexes are not true chemical compounds. According to Dewar, all the above facts are due to the formation of π -complexes between an acid or Lewis acid and the entire π -electron system of an unsaturated compound which should be considered as Lewis base. Because in these complexes a double bond is an electron donor and Lewis acid is an electron acceptor, they are known as donor-acceptor complexes. The decrease in energy in complexing is conditioned by quantum-mechanical reasons.

For each given acid or Lewis acid (electron acceptor), the capacity of an unsaturated system (electron donor) to form a π -complex is proportional to its basicity (donor force), see series (2). At the same time, the increase in relative reactivity of these compounds with respect to electrophilic attack is observed in the similar sequence [34].

Electrophilic substitution in an aromatic series is a biomolecular process which involves displacement of a hydrogen atom bonded to the aromatic ring, acid or Lewis acid.

Experimentally, the mechanism of electrophilic substitution is a two-stage process. The reagents, Lewis base and acids or Lewis acids react correspondingly to form a π -complex which is isomerized to a chemical compound in a slow reaction [34]:



where $X^{(+)}$ – acid or Lewis acid, ArH – Lewis base, $X-Ar^{(+)}-H$ – π -complex, B – base.

As any chemical process, electrophilic substitution of hydrogen in an aromatic ring is a multiple-factor process. Analysis of the factors are beyond the scope of the present work. However there exist theses which have a common importance for chemical reactions. The stage at which a chemical process is stabilized depends on the energy state of resulting products and initial reagents.

In particular, while toluene reacts with nitric acid to form a new chemical compound, the interaction of the same toluene with a C_{60} molecule (Lewis acid is weaker than HNO_3) is terminated at an intermediate stage to form the π -complex $C_{60}^{(-)}-Ar^{(+)}-H$.

The found parallels between donor activity in a series of aromatic hydrocarbons, fullerene solubility in these hydrocarbons and their reactivity relative to electrophilic attack (series 2) will become regular if the process of C_{60} dissolution in aromatic hydrocarbons is considered as an intermediate stage for the reaction of electrophilic substitution in an aromatic series.

9. Conclusions

1. The comparative study of literature data has revealed the parallels between donor force of alkyl derivatives of benzene and their dissolving power relative to C_{60} fullerene.
2. It has been established that C_{60} solubility in methyl derivatives of benzene increases with increasing number of methyl groups in the benzene ring only in the cases that they occupy *ortho*- or *para*-positions.
3. It has been established that if methyl groups are in the *meta*-positions, their number does not change C_{60} solubility in benzene.
4. Based on the found correlation between C_{60} solubility in alkyl derivatives of benzene and electron donor force of these benzene derivatives, it has been concluded that C_{60} dissolution in alkyl derivatives of benzene is an intermolecular charge-transfer interaction to form complexes of the donor-acceptor type.
5. The existence of the "charge-transfer absorption band" at 300 nm in the UV region, bright color of the solutions and a number of other factors suggest formation of donor-acceptor complexes in the toluene solutions of C_{60} .
6. The parallels between C_{60} solubility in alkyl derivatives of benzene and reactivity of these derivatives to the reactions of electrophilic substitution have been established. The parallels allow the C_{60} dissolution to be considered as a reaction of electrophilic substitution of aromatic hydrocarbons.
7. It is well known that the reaction of electrophilic substitution of aromatic hydrocarbons is a two-stage process to form π -complexes at an intermediate

stage. This proposition confirms all the above assumptions and makes it possible to conclude that C_{60} dissolution in aromatic hydrocarbons is a typical reaction of electrophilic substitution in an aromatic series. Stabilization of this reaction is accomplished to form a π -complex.

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CONDUCTIVITY OF C₆₀ FULLERENE CRYSTALS UNDER MULTI-STEP DYNAMIC COMPRESSION UP TO 300 KBAR

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Abstract. In the present work the conductivity of fullerene C₆₀ crystals has been measured under smooth shock wave quasi-isentropic loading conditions up to 30 GPa at initial temperature T=293 K. Not monotone behavior of conductivity has been revealed under compression of crystal with pressure increasing: -at first conductivity grows by many orders then it falls very fast. Conductivity increasing is explained by decreasing of bandgap of C₆₀ under compression whereas conductivity decreasing can be explained on the assumption that the energy barrier of polymerization of C₆₀ reduces with pressure increasing approximately in the same measure, as band-gap energy.

Keywords: fullerite, conductivity, shock waves, manganin gauges, quasi-isentropic compression

1. Introduction

In the crystalline state C₆₀ is a semiconductor with an energy gap E_g of about 2 eV. The excitonic absorption edge corresponds to an energy of about 1.7 eV. The C₆₀ molecules are mainly bound by the Van der Waals forces (Young's modulus is about 13.5 GPa). Thus there is an appreciable reduction of distances between neighboring molecules of C₆₀ in a crystal under moderate pressure. It leads to rapid increase of overlapping of electronic shells and, accordingly, to rapid reduction of band-gap because of expansion of filled (valent) and unfilled energy zones. It is possible to expect transition of a crystal to a metal state in a limit.

2. Results and Discussion

In the first part of present work specific conductivity of fullerene C₆₀ crystals has been measured under smooth quasi-isentropic loading conditions up to 15 GPa at initial temperatures T=293 K and 77 K. We have registered the sharp increase of conductivity more than 6 orders of magnitude in a range of pressure from 0 to 15 GPa, Fig. 1. Value of conductivity regains initial properties after dynamic load is removed. The results received testified about sharply decreasing of band-gap of C₆₀ under compression. However the experimental temperature dependence of

conductivity under pressure indicated that band-gap haven't decreased down to zero and the sample compressed to 15 GPa have remained semiconducting. The X-Ray analysis has shown that C_{60} samples under these conditions regain the initial phase state after dynamic compression is removed. Similar, but a little less expressed effects in behavior of conductivity of C_{70} crystals were observed in the hydrostatic compression experiments.

The purpose of the second part of the present research is measurement of conductivity of fullerene C_{60} crystals under high pressures more than at the former experiments to find out metallization C_{60} is possible. In the latest experiments we used a mode of multi-step quasi-isentropic compression of fullerene crystals by series of consecutive flat shock waves which enables us to reach much higher

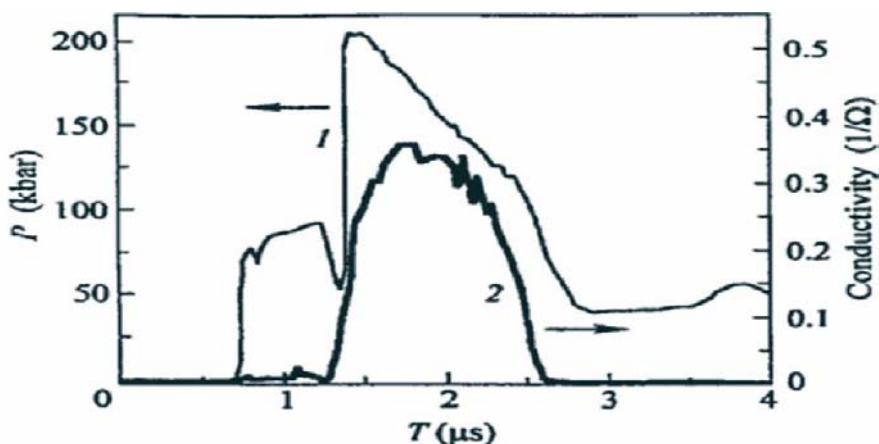


Figure 1. Pressure and conductivity time dependences of the C_{60} crystal under compression by spread shock wave.

pressures without essential warming-up of sample that is common for compression by a unitary shock wave. The idea of the method is as follows presented in [1]. The fullerite sample, which has the form of a rectangular plate with dimensions $8 \times 3 \times 1$ mm and also piezoresistive manganin pressure sensor, are placed between two metal plates (basis and reflector) separated from the sample by 1 mm thick teflon film. Dynamic compression of the sample was carried out by series of the shock waves circulating between the basis and the reflector which was initiated by hit of the steel plate accelerated up speed about 2-2.5 km/s by a special explosive equipment.

The result of typical experiment of measurement of conductivity of C_{60} under multi-step quasi-isentropic compression up to final pressure ~ 30 GPa is presented on Fig. 2 as time dependences of sample conductivity and pressure, measured with help of manganin-foil pressure sensor. It is visible as we can see that at the beginning conductivity of a sample sharply increases and then starts to decrease smoothly despite of proceeding increase of pressure. As against to range 0-15 GPa

change of the kept samples roentgenograms was observed after higher pressure loading (up to 30 GPa). The complex structure of samples transformations were found out at them.

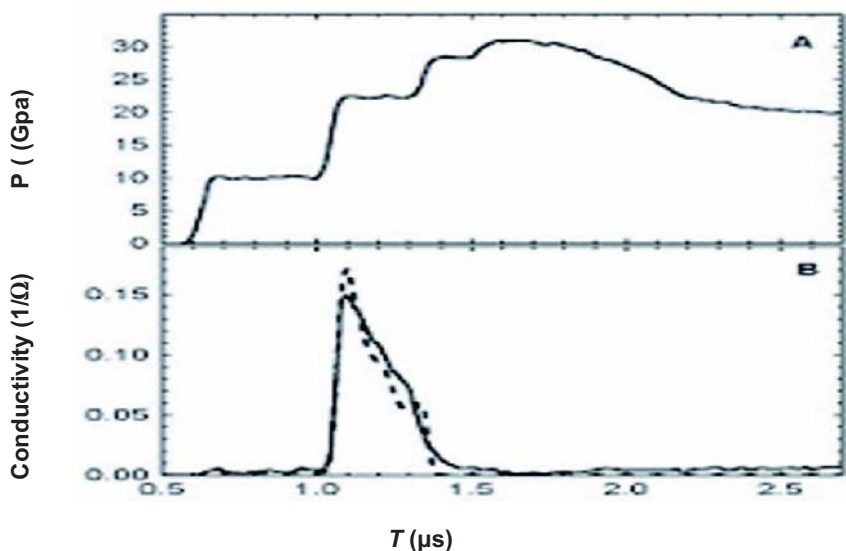


Figure 2. Pressure and conductivity time dependences of the C_{60} crystal under compression by series of the consecutive shock waves.

3. Conclusions

The most essential fact received in the present work that is that at increase in pressure from above 20 GPa conductivity of the sample instead of the further increase on the contrary starts to fall, that formally corresponds to increase in size of effective band-gap energy E_G . It can be connected with phase transformations occurring in system and it is in agreement the data of X-Ray research.

Fundamental fact [2-5] is that at pressures higher than $P_0=0.5-1$ GPa according to polymeric phase C_{60} which is characterized by formation of covalent bonds between molecules of C_{60} becomes thermodynamically preferable. Thus experimental data obtained can be explained with the assumption that energy barrier of C_{60} polymerization becomes lower with pressure increase about equally the band-gap energy.

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GAS INTERSTITIAL FULLERENES PRECIPITATED FROM THE SOLUTION OF C₆₀ IN 1,2-DICHLOROBENZENE

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Abstract. Gas interstitial fullerenes was produced by precipitation of C₆₀ from the solution in 1,2 dichlorobenzene saturated by O₂, N₂, or Ar. The structure and chemical composition of the fullerenes was characterized by X-ray powder diffraction analysis, FTIR spectroscopy, thermal desorption mass spectrometry, differential scanning calorimetric and chemical analysis. The images of fullerene microcrystals were analyzed by SEM equipped with energy dispersive X-ray spectroscopy (EDS) attachment. Thermal desorption mass spectrometry and EDS analysis confirmed the presence of Ar, N and O in C₆₀ specimens. From the diffraction data it has been shown that fullerite with face centered cubic lattice was formed as a result of precipitation. The lattice parameter a_0 was found to enhance for precipitated fullerene microcrystals ($a_0 = 14.19 - 14.25 \text{ \AA}$) in comparison with that for pure C₆₀ ($a_0 = 14.15 \text{ \AA}$) due to the occupation of octahedral interstices by nitrogen, oxygen or argon molecules. The phase transition temperature and enthalpy of transition for the precipitated fullerene microcrystals decreased in comparison with pure C₆₀. Low temperature wet procedure described in the paper opens a new possibility to incorporate chemically active molecules like oxygen to the fullerene microcrystals.

Keywords: Fullerene, doping, infrared spectroscopy, mass spectrometry, X-ray diffraction, crystallite size, lattice constant, gas storage, phase transitions.

1. Introduction

Assink et al [1] have pointed out that fullerenes may provide an efficient way for gas storage. Usually gas C₆₀ interstitial compounds are produced by hot pressing the fullerene solid (fullerite) at temperatures between 200 – 550°C and under gas pressures in the range 170–200 MPa for set periods from 12 to 60h. With this method Ar, Kr and Xe[2] as well as CO [3], CO₂ [4] and N₂O [5] fullerene compounds were produced.

In this paper we report the formation and characterization of the gas interstitial fullerenes of C_{60} with argon, nitrogen or oxygen molecules produced from the solution of C_{60} in 1,2 dichlorobenzene saturated with these gases at room temperature. We used isopropyl alcohol adding for the precipitation of fullerenes from the solution. The choice of this system was dictated by the following reasons: a) the solubility of C_{60} in 1,2 dichlorobenzene is high enough (27 mg/ml [6]), and therefore we do not need too much alcohol for precipitation of fullerenes; b) according to the preliminary experiments isopropyl alcohol was selected for precipitation since it has shown a more stable yield of perfect fullerene microcrystals in comparison with other precipitators like methyl alcohol, ethyl alcohol and the mixture of ethyl alcohol with water. The influence of gas molecules dissolved in solution on the process of fullerene crystallization for the solution is not still clear. The structure and chemical composition of the precipitations was characterized by X-ray powder diffraction analysis, FTIR spectroscopy, thermal desorption mass spectrometry, differential scanning calorimetric and chemical analysis. Thermal desorption mass spectrometry analysis confirmed the presence of Ar, N and O atoms in C_{60} specimens. We discuss the effects of gas intercalation on the lattice parameters and phase transition temperature of precipitated fullerene microcrystals.

2. Experimental

C_{60} (99.5%) purchased from TermUSA, Berkeley, CA was sublimated in vacuum before use [7] and formed fcc lattice ($a_0 = 14.15 \text{ \AA}$). The isopropyl alcohol was distilled under waterless potassium sulfate. The 1,2 dichlorobenzene was purified by sulfuric acid and distilled.

The solution of the fullerene (1mg C_{60} per 1ml 1,2 dichlorobenzene) in a glass retort was fasten on the massive stand to avoid any vibration, and left for 10 days in air, nitrogen, oxygen or argon atmosphere at room temperature (295K). After that the isopropyl alcohol in five time's higher volume was slowly added to the solution without shaking. Isopropyl alcohol was previously saturated with appropriate gas by intensive bubbling during 20 minutes. The mixture was then kept for several days at room temperature in darken place. The black bright crystals precipitated from the solution were finally separated by filtration.

Specimens for scanning electron microscopy were prepared by gentle pressing on the surface of aluminum foil. Scanning electron microscope LEO-1450 (CARL ZEISS) equipped with INCA Energy 300 (OXFORD INSTRUMENTS) attachment was used for imaging and quantitative energy dispersive X-ray spectroscopy (EDS) analysis. The analyzing depth of EDS was 0.1- 0.2 μ . and analyzing area was $25 \times 25 \mu^2$.

X-ray diffraction patterns were taken on DRON (Russia) diffractometer with CuK_α monochromatic radiation at room temperature.

Mass-spectra of the gases eliminated from the specimens under elevated temperature were taken on mass-spectrometer MI-1201B (Sumy, USSR). The gas in ion source was ionized by electron impact (electron energy 70eV). Samples were placed in the quartz ampoule equipped by adjustable heater and connected through the needle valve with inlet system of mass-spectrometer. The sample was pumped out during one day up to the pressure $2 \times 10^{-5} \text{ Pa}$ to remove weakly bounded surface

impurities and contamination. Then the ampoule with the sample was isolated from the pumping system heated and kept at the temperature T_1 for 3 hours. Finally the needle valve was opened and the gases evolved from the sample were analyzed by mass-spectrometer. This procedure including pumping and heating was performed three times at the temperatures $T_1 < T_2 < T_3$.

DSC analysis was performed on DSC 822 (Mettler-Toledo) instrument with "STAR^{cs}" software package. Samples (3-10 mg) were placed in aluminum pans with perforated lids under flowing dry argon (50 ml min^{-1}). The temperature range selected for these measurements was 240K - 410K, at a heating rates 5 and 10K/min.

IR spectra were taken through KBr pellets made by pressing a mixture of fullerene with dry fine powder of KBr. The spectra were measured with 4 cm^{-1} resolution using FTIR spectrometer Perkin-Elmer Spectrum BX-II (USA).

The concentration of Cl in the samples was measured by standard chemical procedure (Schöniger's method) based on decomposition of analyzing compound by burning it in the glass retort [8]. The mixture of caustic potash and hydrogen peroxide was used as an absorbent. The content of Cl in absorbent was detected by mercurous titration.

3. Results and Discussion

3.1. SEM IMAGING AND EDS ANALYSIS

There are two methods for the precipitation of fullerenes from the solution: slow evaporation of the solvent and addition of precipitator which does not dissolve the fullerene but miscible with the solvent. The first method is commonly used (see, for example, [9]) but the second one was applied for precipitation of fullerenes only recently [10,11]. The C_{60} in the solution forms stable aggregates containing fullerene molecules. These aggregates may serve as crystallization centers during precipitation. It would be expected that crystals formed under slow oversaturation of the solution should have the same structure as nucleating centers. The structure of the aggregates and the influence of gas molecules dissolved in the solution on the formation of aggregates are not still clear. The kinetics of aggregation was studied by light scattering method [12]. It was found that the radius of aggregates reaches about 100 nm after 10 days space-hold storage of the solution at room temperature but then the growth rate decreases (radius amounts to about 170 nm during next 100 days). The presence of aggregates or clusters in the solutions of fullerenes was found also by the other authors [13-17]. On the other hand the formation of solvates $C_{60}(\text{Sol})_n$ (where Sol is a solvent molecule) was found after evaporation of the solutions of fullerenes in aromatic solvents [18,19]. The crystallization of these solvates leads to the formation of monoclinic or triclinic lattice [19].

Figure 1 shows scanning electron microscopy (SEM) photograph of microcrystals precipitated from C_{60} solution in 1,2 dichlorobenzene. The mixture of perfect crystals with the size up to 100μ with submicron microcrystals and amorphous clusters represent the typical structure of precipitated fullerenes. It was found that the ratio of the crystalline and amorphous phases depends on the precipitation rate and the temperature of C_{60} solution. The higher crystalline fraction was obtained at lower-temperatures and lower rate of precipitation.

The results of EDS analysis obtained at two different points marked in the Fig. 1 are presented in the Table 1. The first point was selected in the crystalline region and the second one in the amorphous fraction. It is clear that Ar molecules are mainly concentrated in the crystalline region while DCB molecules containing Cl atoms are located preferably in amorphous phase. It is necessary to note that the absolute quantity of Ar obtained by EDS analysis and shown in Table 1 should be considered as a low limit estimation. Thermal desorption of Ar atoms as a result of electron beam heating leads to the reduction of measurement value during analyzing procedure.



Figure 1. Scanning electron microscopy image of fullerene microcrystals precipitated from C_{60} 1,2 dichlorobenzene solution saturated with argon.

TABLE 1. X-ray energy dispersive analysis of Ar interstitial fullerene

Analyzing area (Fig. 1)	C at%	Cl at%	Ar at%
1	99.86	0.10	0.04
2	99.64	0.36	0.00

3.2. X-RAY POWDER DIFFRACTION ANALYSIS

Figure 2 shows the room temperature diffraction pattern for pure C_{60} and for fullerenes precipitated from air and Ar saturated solutions. The X-ray diffraction patterns were taken over a 2θ range of $6 - 60^\circ$. It is clear that the X-ray diffraction patterns of fullerenes contain all the narrow peaks characteristic for face centered

cubic lattice of C_{60} . The intensities of the diffraction peaks for fullerenes are nearly the same as for pure C_{60} . The size of microcrystals in the direction perpendicular to the plane $[hkl]$ was estimated from the equation [20]:

$$D_{hkl} = \lambda / \beta_{hkl} \cos \Theta_{hkl}$$

where λ - is a X-ray wavelength, β - is a full width at half maximum of diffraction peak.

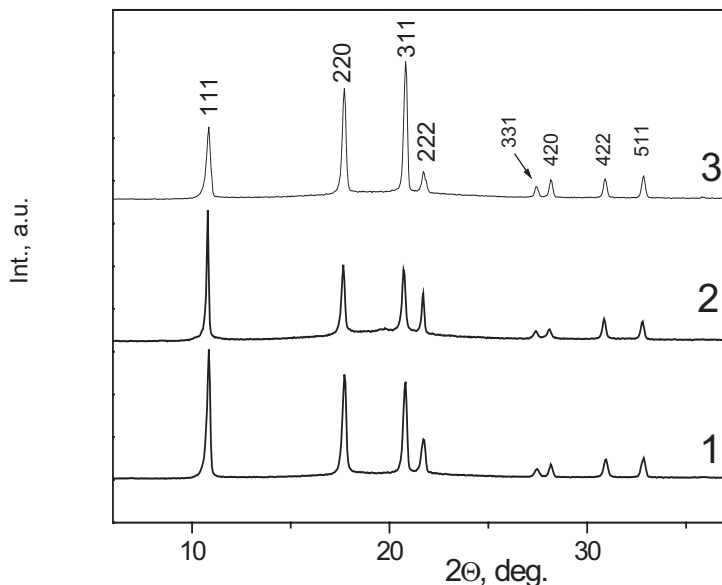


Figure 2. X-ray diffraction patterns from pure C_{60} obtained by vacuum sublimation (1), and precipitated from C_{60} 1,2 dichlorobenzene solutions saturated with air (2) and argon (3).

Table 2 shows that the size of microcrystals is higher for precipitated fullerene than for C_{60} . The diffraction peak (111) has a shoulder at a lower angle, which is more pronounced for precipitated fullerene. According to [21] the asymmetric shape of (111) peak and the appearance of small peak marked by asterisk on the Fig. 2 could be associated with the distortion caused by the formation of two layer extrinsic hexagonal lattice in terchanged with normal fcc lattice of C_{60} . The lattice parameter of precipitated fullerene calculated from the X-ray diffraction pattern $a_0 = 14.19$ Å is distinctly larger than that for pure C_{60} ($a_0 = 14.15$ Å). Most probably the gas atoms occupied octahedral lattice sites during crystallization and caused the lattice parameter increase observed in Ar, O_2 or N_2 fullerenes in comparison with pure C_{60} .

TABLE 2 Dimensions of fullerene microcrystals

Sample preparation	D ₁₁₁ , nm	D ₂₂₀ , nm
Precipitation from the solution	86	50
Vacuum sublimation	79	46

3.3. FTIR SPECTROSCOPY

The IR transmission spectra (Fig. 3) of the fullerene precipitated from the solution saturated with air show four predominant absorption peaks at 526.7, 576.2, 1182.7 and 1429.7 cm^{-1} that could be attributed to the IR active vibration modes (F_{1u}) of the C_{60} molecule with high symmetry (I_h). The IR spectra of 1,2 dichlorobenzene and isopropyl alcohol are also presented on Fig. 3 for comparison. The appearance of the IR bands with the peaks at 746.2, 1034.4, 1126.1, 1249.6 and 1454.2 cm^{-1} confirmed the presence of 1,2 dichlorobenzene in the fullerene (see spectra 1 and 2, Fig. 3). At the same time no visible bands corresponding to the isopropyl alcohol were observed in the IR transmission spectra (see spectra 2 and 3, Fig. 3). There is a peak at 1537 cm^{-1} that is still difficult for interpretation. In fact, precipitation leads to the introduction of mainly solvent molecules but not the molecules of precipitator in the structure of fullerene.

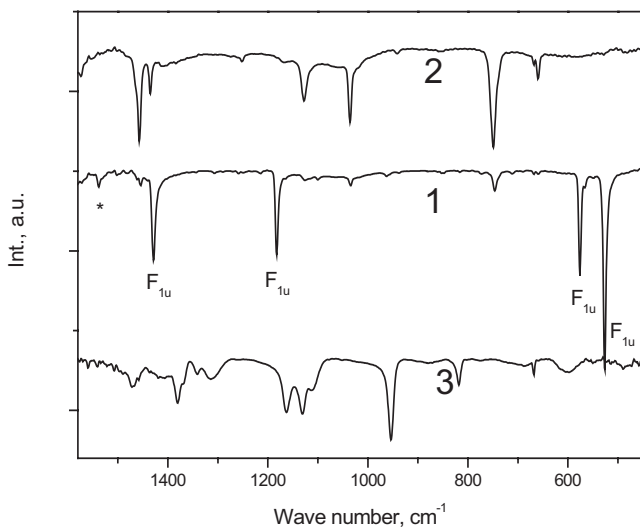


Figure 3. FTIR spectra of fullerene precipitated from the solution saturated with air (1), 1,2 dichlorobenzene (2) and isopropyl alcohol (3).

3.4. MASS-SPECTROMETRY ANALYSIS

To confirm the presence of gas molecules in the fullerene crystals we used thermal desorption mass spectrometry analysis. Before each measurement the sample was held for fixed periods of 3 h at temperatures 65, 150 and 270°C in enclosed quartz

ampoule. Figure 4 shows thermal desorption mass spectra for the fullerene precipitated from the solution saturated with air. The most intensive peak in all mass spectra is $m/z=45$. This peak could be attributed to the isopropyl alcohol fragment $[C_2H_5O]^+$ since all the other peaks characteristic for IPA are present in the mass spectra and the relative intensity of these peaks is close to that in pure IPA: $m/z = 15(4)$; $19(6)$; $27(12)$; $29(7)$; $31(5)$; $39(5)$; $41(7)$; $43(11)$; $45(100)$; $59(5)$. The relative intensities are shown in the parenthesis.

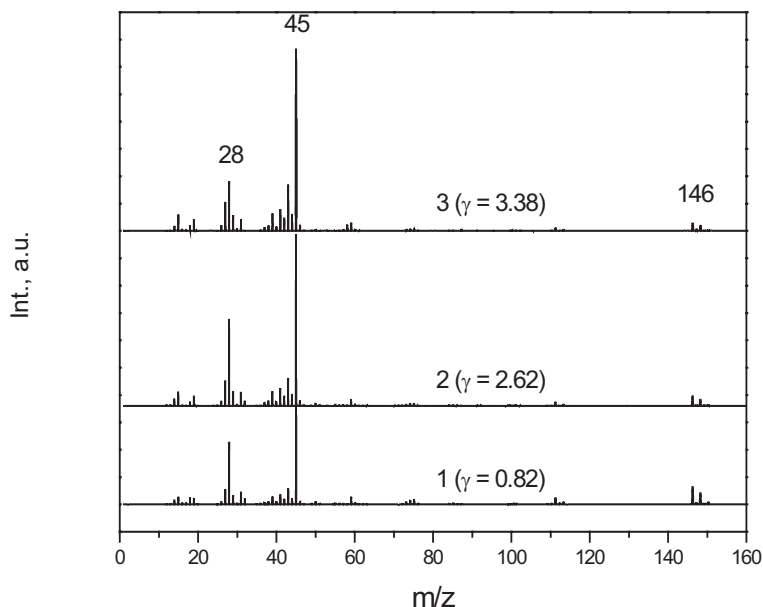


Figure 4. Thermal desorption mass-spectra of fullerene precipitated from the solution saturated with air for the temperature regions: 23-65°C (1), 65-150°C (2) и 150-270°C (3).

The presence of DCB is proved by the appearance of other set of peaks in the mass spectrum at $m/z = 50(10)$; $51(4)$; $73(5)$; $74(8)$; $75(21)$; $111(37)$; $113(12)$; $146(100)$; $147(7)$; $148(65)$; $149(5)$; $150(10)$ with much lower intensities in comparison with these observed for IPA. Using different mixtures of pure IPA and DCB we calibrated the relative intensities of the peaks $m/z=45$ and $m/z = 146$ for our experimental conditions. Based on this calibration and experimental mass spectra we calculated the ratio of IPA/DCB (γ) for gas mixtures eliminated from the fullerene at different temperatures. The γ value increased with the increase of temperature (see Fig. 4) remaining, however less than it was used for precipitation of fullerene from the liquid phase ($\gamma=7.37$). It means that mainly molecules of DCB but not IPA are incorporated into the substances under study. This is in agreement with the IR data discussed earlier. (Fig. 3).

The second intensive peak appeared in all spectra is $m/z = 28$ (see Fig. 4). We suggested that this peak is attributed to the N_2^+ ions because which N_2 molecules

are present in the solution and could be incorporated into C_{60} crystalline structure during precipitation. To prove this assumption we used ultrasonic mixing to intensify the effect of N_2 incorporation during precipitation. As a result of mixing the peak $m/z = 28$ become the most intensive in the mass spectra (see Fig. 5 spectrum 1) of precipitated fullerene. The second intensive peak in this case was $m/z = 32$ (O_2^+). Furthermore, bubbling of C_{60} solution with Ar during precipitation led to disappearance of the peak at $m/z = 32$ in the mass spectra and appearance of the peak at $m/z = 40$ (Ar^+) as the most intensive line in the spectrum (Fig. 5, spectrum 2). However the peak at $m/z = 28$ is still detected in the mass spectrum indicating the presence of nitrogen in the Ar precipitated fullerene structure. It is important to note that rather high temperatures are required for thermal desorption of Ar from our fullerene crystals. Noticeable concentration of Ar was detected in the Ar precipitated fullerene up to 400°C . At the same time the Ar containing C_{60} crystals obtained at the temperatures between $200 - 550^\circ\text{C}$ and under gas pressures in the range $170 - 200$ MPa completely loose the Ar at the temperatures 280°C [2]. Probably incorporation of Ar at high pressure and high temperature leads to the size reduction of C_{60} crystallites thus facilitating the thermal diffusion of Ar at lower temperatures. In our wet procedure larger crystallites are formed.

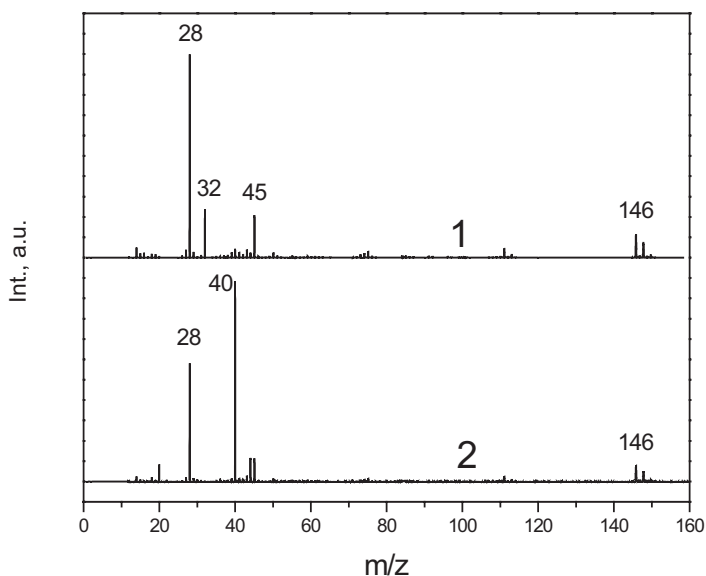


Figure 5. Thermal desorption mass-spectra of fullerenes precipitated from the solution saturated with air (1) and Ar (2). Temperature region $100 - 200^\circ\text{C}$.

3.5. CL CHEMICAL ANALYSIS

The chemical analysis indicated that precipitated fullerene contains about 1.4 wt% of Cl, what is equivalent to 3wt% of DCB. This amount of DCB corresponds to the stoichiometric ratio $(C_{60})_7 (DCB)_1$. The question is where in the fullerene such a

significant amount of solvent molecules could be localized? The Van der Waals volume of the octahedral site $V_{oh} = (4/3)\pi(R_{oh})^3 = 36.6 \text{ \AA}^3$ [1, 22]. The corresponding volumes of DCB and IPA could be calculated from the equation: $V_i = M/(d \cdot N_A)$, where M is a molecular weight, d is a specific density and N_A is an Avogadro constant. According to this calculations $V_i = 186.8 \text{ \AA}^3$ and $127.1 \text{ \AA}^3$ for DCB and IPA molecules respectively. It means that at room temperature, there would exist no space for solvent or precipitator molecules to be incorporated inside the fcc C_{60} lattice without destruction. According to the diffraction data and DSC results described above, precipitated fullerenes do not contain a solvate structures, which are characterized by monoclinic or triclinic low symmetry lattice [19] and melting transitions at temperature region 320 – 340K [18]. According to EDS analysis DCB molecules are preferably concentrated in the amorphous phase. Most likely the DCB and IPA molecules are concentrated in the intercrystalline caverns similar to that observed in the zeolites [23]. The presence of caverns formed by graphitic sheets with negative Gaussian curvature was also observed in amorphous carbon [24]. The further research is needed to answer this question.

3.6. DSC MEASUREMENTS

Weak Van der Waals (VDW) forces do not prevent the C_{60} molecules from freely rotating at room temperature [25]. However, cooling and reducing of the thermal energy to the value comparative with VDW interaction allows locking of C_{60} molecules into fixed orientation with respect to each other. Thus, the C_{60} lattice undergoing an orientational ordering phase transition from face centered cubic Fm3m to simple cubic (sc) Pa3 [26]. Intercalation of gas molecules into C_{60} lattice would influence the VDW forces and, as a result, decrease the temperature at which orientational ordering takes place [2]. Figure 6 shows the DSC curves obtained for pure C_{60} and C_{60} precipitated in the presence of air, oxygen and Ar. Table 3 shows the phase transition temperatures and enthalpy of transitions. The gas intercalation causes the shift of order-disorder transition peak detected for pure C_{60} at 263K to the lower temperatures for precipitated fullerenes. This effect implies that lower temperatures are required to bring about orientational ordering when the lattice is expanded by intercalation of different gases. The decrease of the enthalpy value normalized to the weight of the sample for intercalated fullerenes in comparison with pure C_{60} may be due to the presence of amorphous phase in precipitated fullerenes.

TABLE 3. DSC analysis of gas interstitial fullerenes

Sample	Peak temp.(K)	$\Delta H \text{ (Jg}^{-1}\text{)}$
Pure C_{60}	263,1	8,0
$Ar_x C_{60}$	254,8	5,7
$(N_2)_x(O_2)_y C_{60}$	257,7	2,8
$(O_2)_x C_{60}$	254,5	5,9

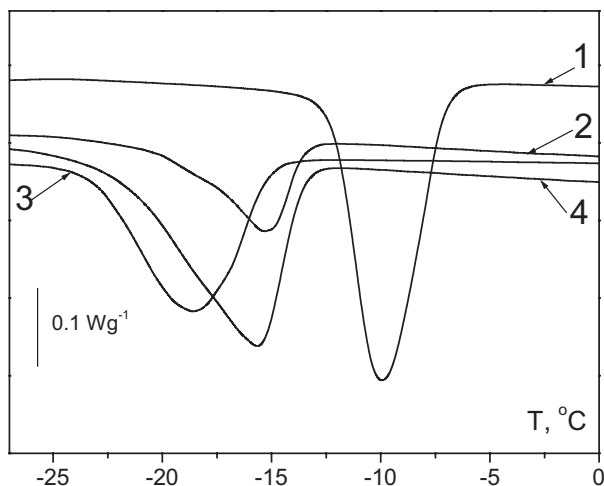


Figure 6. DSC curves for pure C_{60} , (1) and fullerenes precipitated from the solution saturated with air (2), Ar (3) and O_2 .

4. Conclusion

The wet procedure described above and based on precipitation of microcrystals from the solution makes possible to introduce gas molecules in the lattice of C_{60} at room temperature and atmospheric pressure. In contrast to hot pressing method, which could be used only for incorporation of chemically inert molecules to the fullerenes, low temperature technique allow us to synthesize for the first time fullerene microcrystals containing chemically active molecules like oxygen. The molecules of O_2 , N_2 and Ar atoms occupy octahedral lattice sites in C_{60} microcrystals causing the lattice parameter increase. Ar interstitial fullerene obtained by precipitation was found to exhibit much higher thermal stability then that produced by hot isostatically pressing method.

Acknowledgements

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Mg₂NiH_x AS PROCATALYST OF SYNTHESIS OF CARBON NANOFIBERS

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Abstract. It was established that powdered Mg₂NiH_x is effective procatalyst of synthesis of carbon nanofibres. The maximal yield on soot is reached at 500°C, and an optimum ratio of gas components in a mixture for the maximal yield is C₂H₄:H₂:Ar = 1:1.25:1.25.

Keywords: Intermetallide; Ethylene; Procatalyst; Pyrolysis; Carbon nanofiber

1. Introduction

Among a wide number of metal catalysts used for the synthesis of carbon nanofibres (CNF) and nanotubes (CNT) in the processes of pyrolytic decomposition of hydrocarbons nickel is by one of the most effective catalysts [1–3]. As the diameter of such carbon tubular products essentially depends on the size of catalytic particles [3–6], to synthesize CNF and CNT of less thickness in most cases the presence of catalyst in the form of nanosized metal particles is required in the reaction zone, and the particles being not subjected to agglomeration and sintering. To reach this goal it was offered to use the intermetallic compounds of nickel, in particular LaNi₅ and LaNi₂ [7–8], where at the certain chemical treatment (the etching in alkali) of intermetallide powder and at subsequent reduction of nickel oxide by hydrogen on a intermetallide surface a phase of metallic nickel is formed in the form of small particles serving subsequently as the catalyst of hydrocarbon pyrolysis and growth of CNF.

In the work of CNF synthesis by decomposition of hydrocarbon gases over intermetallic compounds of La and Ni, made by us earlier, it was shown, that the particles of metal nickel can be formed directly during pyrolysis reaction [9].

In the present work the decomposition of hydrocarbons was carried out at presence of intermetallide hydride Mg₂NiH_x as high-dispersed powder which was received by hydride dispergation of an initial alloy. The work is aimed at finding correlation between process parameters (temperature, composition of gas phase) varied in a wide range and the contents of carbonaceous products.

The obtained carbon nanofibers were used for the synthesis of composite materials $\text{MgH}_2\text{-CNF}$, whose hydrogen storage characteristics were thoroughly studied.

2. Experimental

The pyrolysis of ethylene was carried out in a cylindrical horizontal flow gas reactor (length – 800 mm, diameter – 40 mm) (Fig. 1) in a range of the temperatures 400–800°C (in a zone of reaction) under pressure of 0.1 MPa. A powder of Mg_2NiH_x with the size of particles of 1–10 μm was received by 10-multiple recurrence of cycles "hydrogenation-dehydrogenation" of an alloy of appropriate intermetallide [10]. In all experiments LaNi_5H_x in weight 0.1 g was settled down as a thin stratum having the thickness of 0.3 mm at the bottom of quartz floater, which was placed in the reactor center. The gaseous mixtures $\text{C}_2\text{H}_4/\text{H}_2/\text{Ar}$ were used at various ratios. The feed rate of ethylene was constant in all experiments – 40 cm^3/min , as well as the total flow rate of the gas mixture – 140 cm^3/min . The gas phase composition was varied by changing the volumetric rates of gas flows H_2 and Ar within the range of 0–100 cm^3/min . The detailed description of the experiment is provided elsewhere [9]. The duration of the process was 1 h in all experiments. The only soot formed during 1 h on the surface of powdered intermetallide was taken into account while determining the mass of carbon products of the pyrolysis.

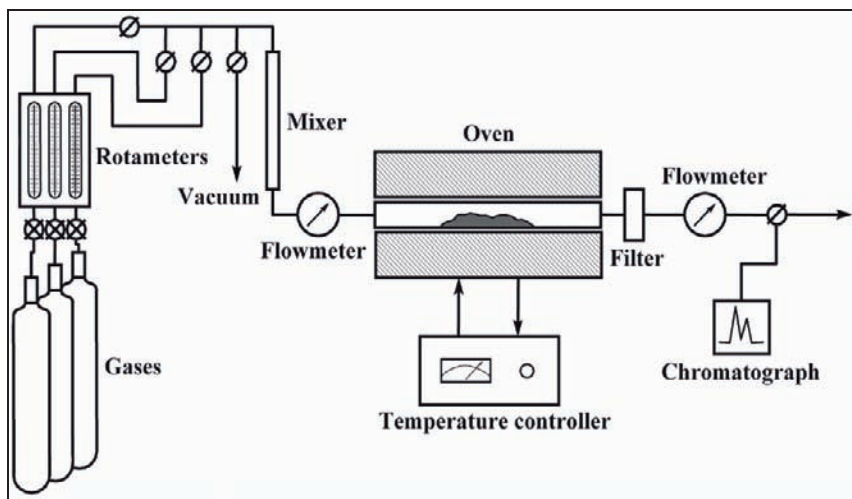


Figure 1. Experimental setup for pyrolytic synthesis of carbon nanomaterials in the flow gas reactor.

The products of the pyrolysis were investigated by methods of the chemical analysis, transmission electron microscopy (TEM) with use of electronic microscope EMV-100B and X-ray diffraction analysis on installation DRON-1.

3. Results and Discussion

According to the chemical analysis data, the hydrogen content in the synthesis products is within the limits of 0.5 %, while Mg:Ni ratio being close to the initial composition of the intermetallide. X-ray diffraction analysis of the synthesis products testifies to presence in them of metallic nickel particles ($d = 2.04, 1.76 \text{ \AA}$), graphitized carbon ($d = 3.39 \text{ \AA}$), and threefold carbide MgNi₃C ($d = 3.83, 2.21, 1.91$ and $1.71 \text{ \AA}$) (Fig. 2). This means that during the pyrolysis of ethylene the initial intermetallide decomposes to form the threefold carbide and the particles of metallic nickel. On the particles of metallic nickel the process of nucleation and growth of soot carbonaceous products proceeds.

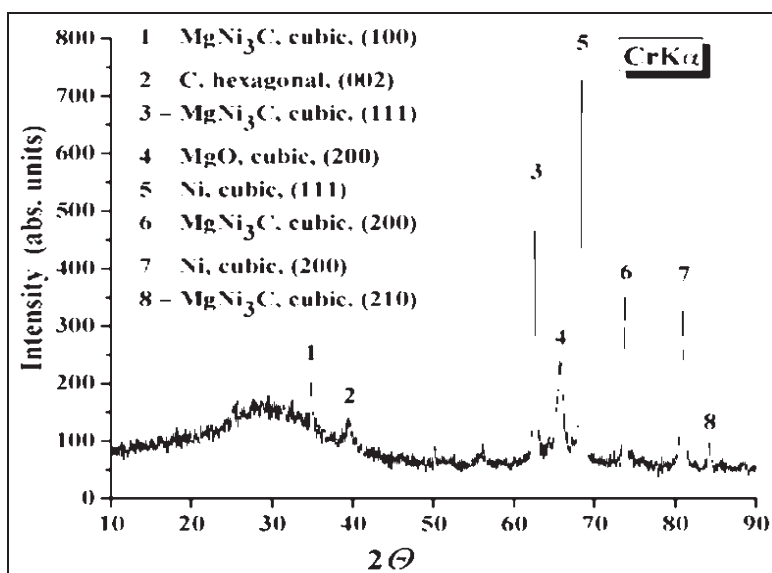


Figure 2. X-ray diffraction data of pyrolysis products, obtained at 700°C.

The appreciable formation of soot was marked already at 400°C (Fig. 3). The greatest yield on the soot was reached at 500°C. With further increasing the pyrolysis temperature the soot mass decreases due to coking of the work surface of catalytic particles. At addition in system of hydrogen increase of weight of soot also was observed, and the maximal yield was moved together in more high-temperature area. Obviously, the hydrogen interacted with the predecessors of coke representing fragments C_xH_y ($x = 1, 2$; $y = 1, 2, 3$), adsorbed on the surface of nickel particles. Thus hydrogen translated such fragments back to the gas phase thus decreasing the amount of amorphous carbon and increasing that of structured fibers. It is clear that further increase of the hydrogen content leads to decrease of the total yield of the soot.

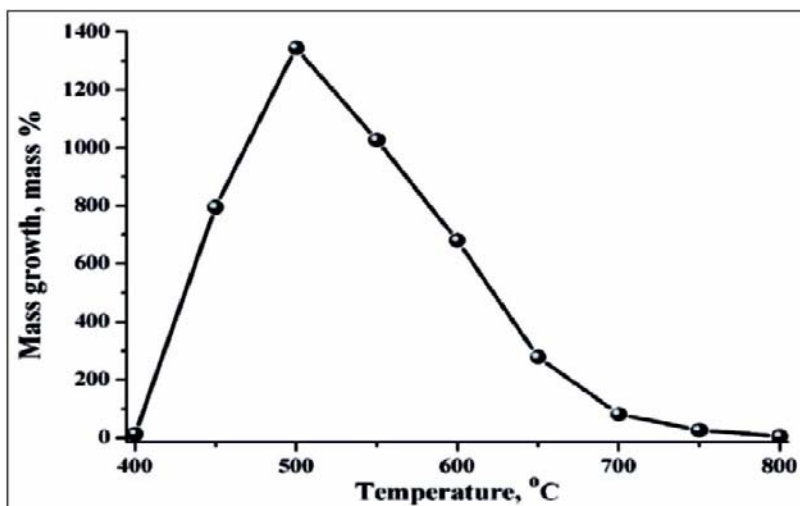


Figure 3. Temperature dependence of the soot mass growth at the gas mixture contents of $C_2H_4:H_2:Ar = 1:1.25:1.25$.

The gas mixture contents of $C_2H_4:H_2:Ar = 1:1.25:1.25$ was determined to be the optimal one for the maximal yield of the soot (Table 1).

TABLE 1. Mass of the soot (g/g Mg_2Ni) formed at various temperatures of C_2H_4 pyrolysis (rate of volume flow of feeding gases $40\text{ cm}^3/\text{min}$) and $Ar:H_2$ ratios

Ar:H ₂ ratios		Temperature, °C			Mass, g
Ar	H ₂	500	600	700	
100	0	0.44	0.15	0.20	
75	25	6.52	6.55	1.04	
50	50	13.44	6.80	0.81	
25	75	11.60	9.67	0.94	
0	100	11.68	12.27	1.91	

The transmission electron microscopy of the pyrolysis products (Fig. 4) shows the presence of carbon fibers having the outer diameter of 20–200 nm, and some of them, the thinnest, having hollow channel inside. The most of fibers are a kind of tightly curled helices or "plumed clouds".

The investigation of hydrogen sorption properties of the MgH_2 -CNF composites, obtained by mechanochemical treatment of mixtures of the components, testifies about availability of use of carbon nanofibers for creation of hydrogen storage composite materials.

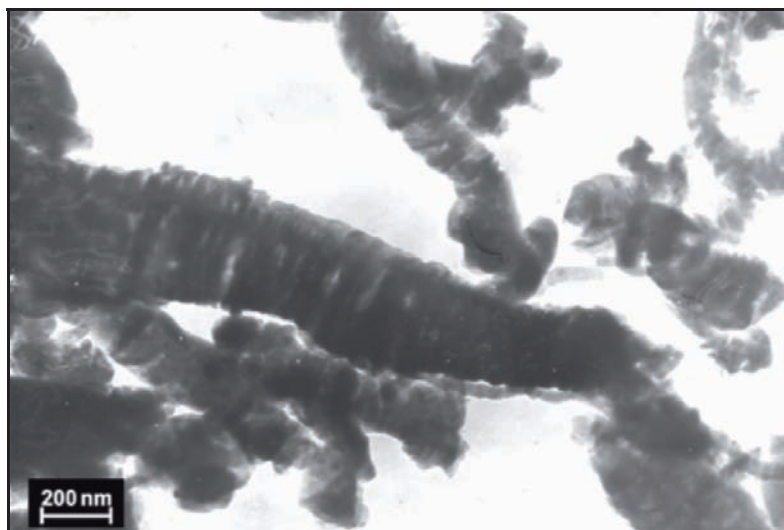


Figure 4. TEM image of nanofibers, obtained at 600°C.

Acknowledgment

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ELECTRONIC STRUCTURE EXPLORATION OF ACTIVE ELEMENT SURFACE FOR HYDROGEN SENSOR BASED ON WO_{3-x} NANOPARTICLES

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Abstract. Nanopowders of nonstoichiometric tungsten oxides were synthesized by method of electric explosion of conductors (EEC). Their electronic and atomic structures were explored by XPS and TEM methods. It was determined that mean size of nanoparticles is $d=10-35$ nm, their composition corresponds to protonated nonstoichiometric hydrous tungsten oxide $WO_{2.91} \cdot (OH)_{0.09}$, there is crystalline hydrate phase on the nanoparticles' surface. After anneal a content of OH-groups on the surface of nonstoichiometric samples is higher than on the stoichiometric ones. High sensitivity of the hydrogen sensor based on $WO_{2.91} \cdot (OH)_{0.09}$ at 293 K can be connected with forming of proton conductivity mechanism.

Keywords: X-ray photoelectron spectroscopy, method of electric explosion of conductors, nonstoichiometric oxides, electronic structure, nanoparticles.

1. Introduction

Nanoparticles of nonstoichiometric tungsten oxides WO_{3-x} are promising material to produce active elements for hydrogen sensors. High work temperature that causes degradation processes is a problem of exploitation of gas sensors based on nanoparticles of semiconductor oxides.

In the work an electronic structure of nanoparticles of nonstoichiometric oxide WO_{3-x} was investigated by XPS-method at room and work temperatures. Hydrogen sensor based on these nanoparticles showed a good sensitivity at room temperature.

2. Experimental

The electronic structure of nanopowders was explored by method of X-ray photoelectron spectroscopy (XPS) by electronic spectrometer ES-2404 with PHOIBOS-100_SPECS energy analyzer ($E_{MgK\alpha}=1253.6$ eV, $P=200$ W, $P=2 \cdot 10^{-7}$ Pa). The spectrometer is equipped with an ion gun IQE-11/35 and a flood gun FG 15/40 for sample charge neutralization. The spectra of $W4f_{7/2}$ -level were factorized into component couples with parameters $\Delta E_p (4f_{5/2} - 4f_{7/2}) = 2.1$ eV, $I_{4f_{5/2}} / I_{4f_{7/2}} = 0.77$. The spectra of $O1s$ -level were factorized into separate components. The factorization was carried out by Gauss-Newton method. The areas of components were determined after subtraction of background by Shirley method [1].

Nanopowders of nonstoichiometric tungsten oxide WO_{3-x} were synthesized by EEC-method. According to the TEM data (Fig. 1) the mean size of nanoparticles is 10-35 nm, size distribution is normal (Gaussian). The nanoparticles have spherical shape, well-defined crystalline structure, their agglomeration is almost absent. The macropowders of stoichiometric tungsten oxide WO_3 was obtained at combustion of metal in oxygen. The macropowders of stoichiometric (sample MS) and the nanopowders of nonstoichiometric (sample NN) tungsten oxides were examined: conditioned on air (samples MS1 and NN1 respectively) and annealed on air at 563 K (samples MS2 and NN2 respectively).

The XPS-spectra of W4f- and O1s-levels of the samples and the results of their factorization into components are shown on Fig. 2 and Fig. 3 and Table 1. The maxima of component couples on Fig. 2 correspond to W4f_{7/2}- and W4f_{5/2}-levels of tungsten atoms in W⁵⁺-states (comps. c-c') [2] and W⁶⁺-states (comps. d-d'/e-e') [2-3]. The maxima of components on Fig. 3 correspond to O1s-levels of oxygen atoms O²⁻ in the lattice (comp. f) [3], OH-groups (comp. g) [3], and various types of H₂O (comp. m) and O_{2 ads} molecules adsorbed on the surface (comp. n) [4-6]. The h-component can form from several contributions, as the signal in this energy range is formed by the O⁻ oxygen states as well as by C=O, O-C-O groups [3, 7-8].

As it can be seen on Fig. 2-1, the surface of macrocrystalline stoichiometric tungsten oxide conditioned on air (sample MS1) is formed of oxide phases WO_3 (comp. d, $E_p\text{W4f}_{7/2}=35.7$ eV) and crystalline hydrate $\text{WO}_3 \cdot (\text{H}_2\text{O})$ (comp.e, $E_p\text{W4f}_{7/2}=36.1$ eV). At the factorization into components of the O1s-line of this sample (Fig. 3-1) the main signal is the one of oxygen atoms O²⁻ of lattice with bonding energy $E_p\text{O1s}=530.6$ eV (comp.f), the presence of OH-groups (comp. g, $E_p=531.1$ eV) and water (comp. m, $E_p\text{O1s}=533,0$ eV) is recorded. After the anneal on air of the stoichiometric oxide macropowder (sample MS2) the signal from crystalline hydrate phase disappears, the surface is completely formed with the oxide WO_3 . Thus on the W4f-spectra (Fig. 2-2) only component d with $E_{\text{bond}}=35.7$ eV is present in the region of the main maximum of W4f-line. O1s-line of this sample (Fig. 3-2) is mostly formed of components' h ($E_p=531.8$ eV) and m (H_2O , $E_p\text{O1s}=533,0$ eV) contributions. In this case the component h can be connected with the C=O and O-C-O groups adsorbed by the surface, the contribution of this component in the samples MS1 and MS2 doesn't change. It can be seen from Fig. 3-2 that after the anneal on air (samle MS2) the signal from OH-groups (comp. g) disappeared.

The surface of the nanocrystalline nonstoichiometric tungsten oxide conditioned on air (sample NN1) is almost completely formed of crystalline hydrate $\text{WO}_3 \cdot (\text{H}_2\text{O})$. Thus on the W4f-spectra (Fig. 2-3) the main component is comp. e with $E_p=36.1$ eV, on the O1s-spectra (Fig. 3-3) along with the O²⁻-states, the contributions from OH-groups (comp. g) and from H₂O (comp. m) are present.

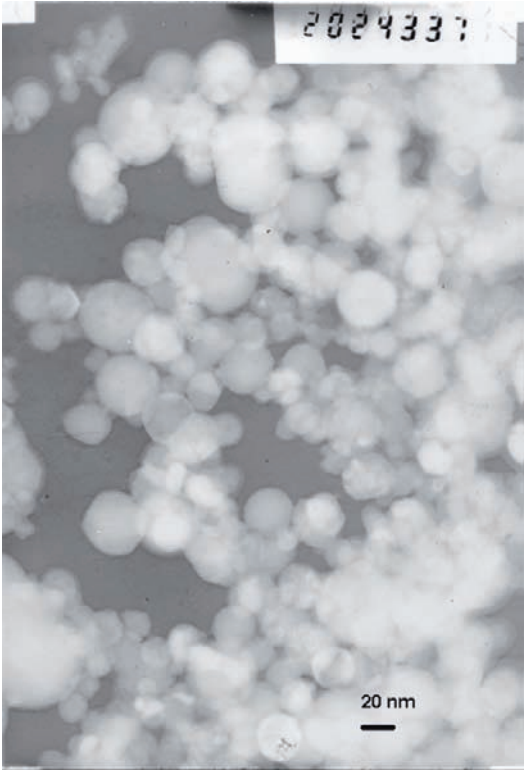


Figure 1. TEM micrograph of nanoparticles.of nonstoichiometric tungsten oxide.

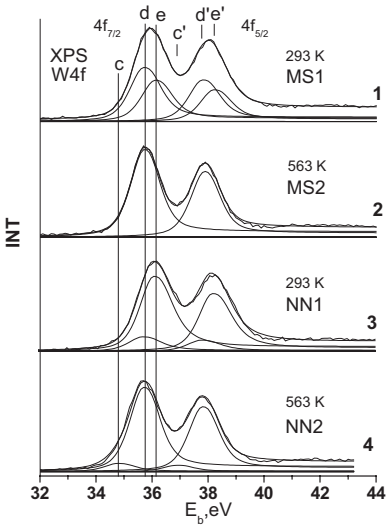


Figure 2. XPS-spectra of W4f-level of tungsten atoms factorized into components for MS1 (2-1), MS2 (2-2), NN1(2-3), NN2(2-4).

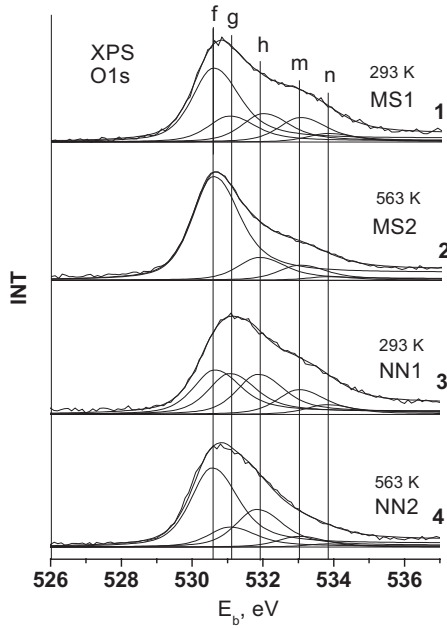


Figure 3. XPS-spectra of O1s-level of tungsten atoms factorized into components for MS1 (3-1), MS2 (3-2), NN1(3-3), NN2(3-4).

After the anneal on air of the nonstoichiometric tungsten oxide nanopowder the signal from crystalline hydrate $\text{WO}_3 \cdot (\text{H}_2\text{O})$ (comp. e) in the spectrum of W4f-level (sample NN2, Fig. 2-4) disappeared. The component d from W^{6+} -states of the oxide dominated in the spectrum of W4f-level after anneal on air and the component c from W^{5+} -states ($E_p \text{W}4f_{7/2} = 34.8 \text{ eV}$) appeared in the low energy region.

Simultaneous appearing of W^{5+} -, W^{6+} -states in the W4f-spectrum are connected with the phase of nonstoichiometric tungsten oxide. Taking into consideration the presence of OH-groups in the sample NN2 and knowing the contributions of W^{5+} -, W^{6+} -states (Table 1) it is possible to determine a coefficient x for matrix $\text{W}_x^{5+}\text{W}_{1-x}^{6+}\text{O}_{3-x}(\text{OH})_x$, which equals $x=0.09$. Thus the sample NN2 can be classified as protonated oxide $\text{WO}_{2.91}(\text{OH})_{0.09}$.

At the comparison of the O1s-spectra of the samples MS2 and NN2 it is seen (Fig. 3-2, Fig. 3-4, Table 1), that after anneal on air the $\text{OH}^-/\text{O}^{2-}$ - ratio in the nonstoichiometric sample of tungsten oxide is higher than in the stoichiometric sample. High concentration of the OH-groups on the active element's surface can form a proton conductivity mechanism and cause a high sensitivity of the hydrogen sensor based on $\text{WO}_{2.91}(\text{OH})_{0.09}$ nanoparticles at 293 K.

TABLE 1^a Peak energies (E_p , eV), relative intensities of the components (I, %) and $\text{OH}^-/\text{O}^{2-}$ - ratio for MS1, MS2, NN1 and NN2 samples

E_p /Sample	MS1, I (%)	MS2, I (%)	NN1, I (%)	NN2, I (%)
c, W^{5+} , $\text{W}4f_{7/2}$ 34.8 eV	-	-	-	8.9
d, W^{6+} , $\text{W}4f_{7/2}$ 35.7 eV	56.7	100	14.2	91.1
e, W^{6+} , $\text{W}4f_{7/2}$ 36.1 eV	43.3	-	85.8	-
f, O^{2-} , $\text{O}1s$ 530.6 eV	45.9	71.5	27.9	52.7
g, OH^- , $\text{O}1s$ 531.1 eV	16.1	-	25.6	13.3
h, O^- , $\text{C}=\text{O}$, $\text{O}-\text{C}-\text{O}$ $\text{O}1s$ 531.8 eV	17.6	15.7	25.1	24.9
m, H_2O , $\text{O}1s$ 533.0 eV	15.1	10.3	15.4	7.1
n, $\text{O}_{2\text{ads}}$, $\text{O}1s$ 533.8 eV	5.3	2.5	6.0	2.0
$\text{OH}^-/\text{O}^{2-}$	0.35	0	0.92	0.25
Precision, ΔI	$\pm 0.9 \div 1.2$			

^a E_p = peak energy; I = relative intensity (total = 100%)

3. Conclusions

- OH-group content on the surface of tungsten oxides depends on their initial nonstoichiometry by oxygen.
- high sensitivity of the hydrogen sensor based on $\text{WO}_{2.91} \cdot (\text{OH})_{0.09}$ nanoparticles at 293 K can be connected with forming of proton conductivity mechanism in them.
- conditioning on air of nanoparticles of nonstoichiometric tungsten oxide leads to forming of crystalline hydrate $\text{WO}_3 \cdot (\text{H}_2\text{O})$ on the surface.
- nonstoichiometry coefficient in the examined tungsten oxides can be determined by the ratio of W^{5+} and W^{6+} cations' contributions.

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ISOTOPIC EFFECT IN HYDROGEN AND NITROGEN SOLID SOLUTIONS IN α -Ti

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Abstract. Neutron diffraction and X-ray diffraction were applied to study the ordering in the $\text{TiN}_{0.26}\text{H}_{0.15}$, $\text{TiN}_{0.26}\text{D}_{0.15}$ and $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ solid solutions. Hydrogen atoms are found to redistribute over octahedral and tetrahedral interstices of the hcp-structure of the $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solution with varying temperature. Consecutive ordering-decay processes and the ordering of antiphase domains are discovered at temperatures below the decay temperature. In a high-temperature disordered state, isotopically different solid solutions $\text{TiN}_{0.26}\text{H}_{0.15}$, $\text{TiN}_{0.26}\text{D}_{0.15}$ have identical structural characteristics; as temperature decreases, an isotopic effect comes into operation. This effect consists of the following: as opposed to the hydrogen solid solution, in the deuterium solid solution ordering starts at a far higher temperature; an ordered monoclinic phase has a larger homogeneous region; interstitial ^2D and ^1H distribution over interstices is different in character; and the blocking effect between interstitial atoms is more pronounced. The displacement of hydrogen atoms from the center of the tetrahedron along the c axis has different signs in the disordered and ordered solid solutions.

Keywords: interstitial solid solutions, crystal structure, phase transformation, order-disorder, isotopic effect, antiphase domains, neutron diffraction, $\text{TiN}_{0.26}\text{H}_{0.15}$, $\text{TiN}_{0.26}\text{D}_{0.15}$, $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$.

1. Introduction

Hydrogen atoms strongly affect the crystal structure and properties of nitrogen and/or carbon solid solutions in α -Ti- TiN_xH_y [1]. Ordering in TiN_xH_y , nitrogen and hydrogen solid solution (ss) in α -Ti, was studied by neutron diffraction [2]. It is of interest are neutron diffraction studies of ordering in TiN_xD_y and $\text{TiN}_x\text{H}_{y/2}\text{D}_{y/2}$. The results of these studies in comparison to the results obtained from TiN_xH_y (ss) can give valuable information about the role of hydrogen and the interaction energy of the strain between interstitial atoms and metal atoms in structure formation and phase relations for hydrogen solid solutions in α -Ti.

This study deals with ordering $\text{TiN}_{0.26}\text{H}_{0.15}$, $\text{TiN}_{0.26}\text{D}_{0.15}$ and $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ solid solutions as probed by neutron diffraction.

2. Experiment

Neutron diffraction patterns of powder samples were taken on a neutron diffractometer ($\lambda = 1.085 \text{ \AA}$) mounted on the thermal column of a VVR-SM nuclear reactor [3]. The DBW-3.2 program for the Rietveld neutron diffraction line shape analysis was used in calculations and structure refinement [4]. A DRON-3M X-ray diffractometer (CuK_{α} - radiation) was used to measure X-ray powder diffraction patterns.

The $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solution sample was prepared by self-propagating high-temperature synthesis from a PTM grade titanium powder containing 0.35 wt % H_2 [2]. $\text{TiN}_{0.26}\text{D}_{0.15}$ solid solution sample was prepared by deuteriding powdered $\text{TiN}_{0.26}$ sample at temperatures from 970 - 370 K by the Sieverts process. The samples were followed by 6 h homogenizing anneals in degassed and sealed silica glass ampoules at 1270 K and by air quenches. Usually, such thermal processing does not change the hydrogen content of a sample [2]. X-ray powder diffraction shows that the solid solutions $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ are single-phase and samples had a hexagonal unit cell with $a = 2.978 \pm 0.002$, $c = 4.795 \pm 0.003 \text{ \AA}$ and $a = 2.983 \pm 0.002$, $c = 4.805 \pm 0.003 \text{ \AA}$, accordingly [2, 5]. $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ solid solution are prepared in equal proportion $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ solid solutions by sintering bath in evacuated and sealed quartz ampoule was sintered under special regime selected by us. The final product was prepared after the annealing at 1270 K (6 hours) followed by quenching in air. Chemical analysis showed that the hydrogen and nitrogen contents of the samples remained practically unchanged upon this processing. According to the neutron diffraction reflections pattern the sample is single-phase and that it has ordering hexagonal structure with the parameters $a = 2.987 \pm 0.007$, $c = 4.839 \pm 0.003 \text{ \AA}$. Divergence in parameters lattice in comparison with parameters lattice of the solid solutions $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ is probably conditioned different mistakes of determination parameter lattices by methods (X-ray and neutron diffraction).

3. Results and discussion

Processing the neutron diffraction reflections pattern (Fig. 1a) for the solid solution $\text{TiN}_{0.26}\text{H}_{0.15}$ quenched from 1270 K showed that all nitrogen atoms randomly occupy octahedral interstices 2 (a) and hydrogen atoms, both octahedral interstices 2 (a) (50 %) and tetrahedral interstices 4 (f) in terms of space group $\text{P6}_3/\text{mmc}$ (the α -phase). After quenching the sample from temperatures in the range, diffuse neutron scattering is observed in the Bragg angle range of $2\theta = 11\text{--}18^\circ$ (Fig. 1b). Long-range ordering corresponding becomes noticeable at 920 – 820 K (12 h, Fig. 1c). The simulation of the neutron diffraction for a sample shows that at this temperatures hydrogen atoms occupy only one type of tetrahedron 2 (d) and that nitrogen atoms are partially disordered, preferring to occupy octahedral positions 1 (a) in terms of space group $\text{P}\bar{3}\text{m1}$ (α' -phase). Longer exposures of up to 28 h at

850 K cause the complete decay of the solid solution into a pair of phases, one with a lower and the other with a higher nitrogen percentage than that in $\text{TiN}_{0.26}\text{H}_{0.15}$. One phase is the ordered α' -phase, and the other is the ordered γ -phase (space group C2/m). Thus, the partially ordered α' -phase in the $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solution is metastable. Between 1170 and 870 K, a cascade of phase

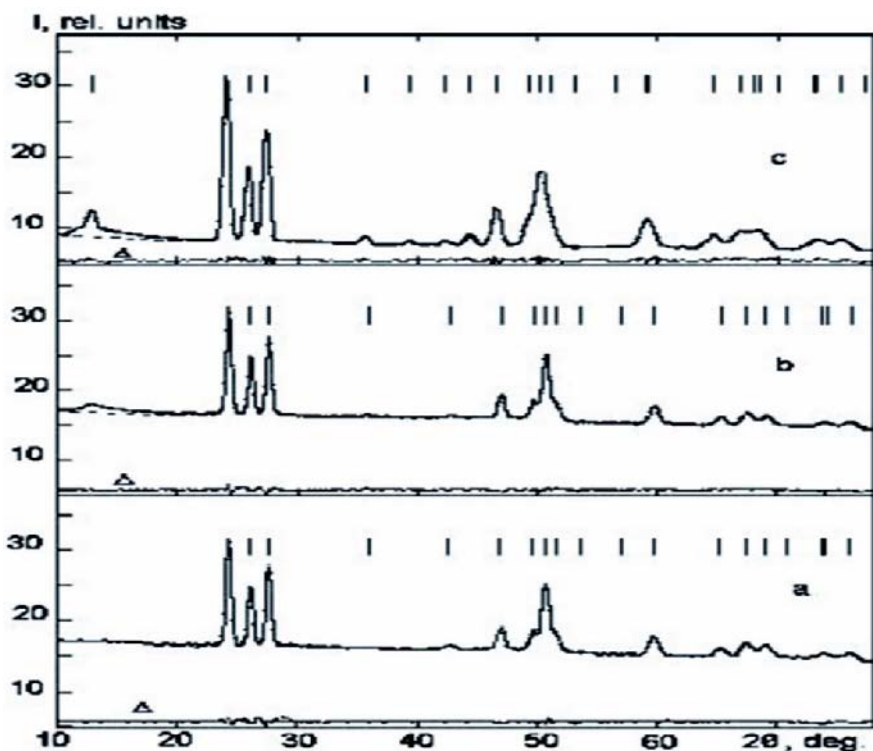


Figure 1. Neutron diffraction patterns of $\text{TiN}_{0.26}\text{H}_{0.15}$, solid solution samples quenched from 1170 K (a); 1070 K (b) and 890 K (c) (points show data points, the solid line is the fitted curve, and $\Delta = I_{\text{exp.}} - I_{\text{calc.}}$).

transitions is observed:

Disorder $\xleftarrow{1170\text{K}}$ Short-range order $\xleftarrow{\approx 1020\text{K}}$ Long-range order $\xleftarrow{870\text{K}}$
Exsolution

or $\alpha \xleftarrow{1170\text{K}}$ α with short - range order $\xleftarrow{1020\text{K}}$ α' $\xleftarrow{870\text{K}}$ $\alpha' + \gamma$.

The above pattern makes it clear that the exsolution is preceded by (partial) long-range order, and that long-range order is preceded by short-range order. However, this is merely a simplified pattern. Actually, the temperature intervals of the existence of short-range order, long-range order, and exsolution overlap. Short-range order exists in the interval of 1170 - 820 K; long-range order exists between

1020 and 740 K; short-range order coexists with long-range order at 1020 – 820 K; and order is changed by exsolution at 850 – 800 K. The dominant process is a function of temperature. The rate at which ordering and exsolution processes change each other is also a function of temperature. If at 850 K signs of decay are observed after 18 h of exposure, at 800 K they appear only after 48 h of exposure.

To shed light on the ordering process in $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss), disordered samples were annealed at various temperatures in the range of 1190 – 740 K, and the state corresponding to each temperature was frozen by quenching in air.

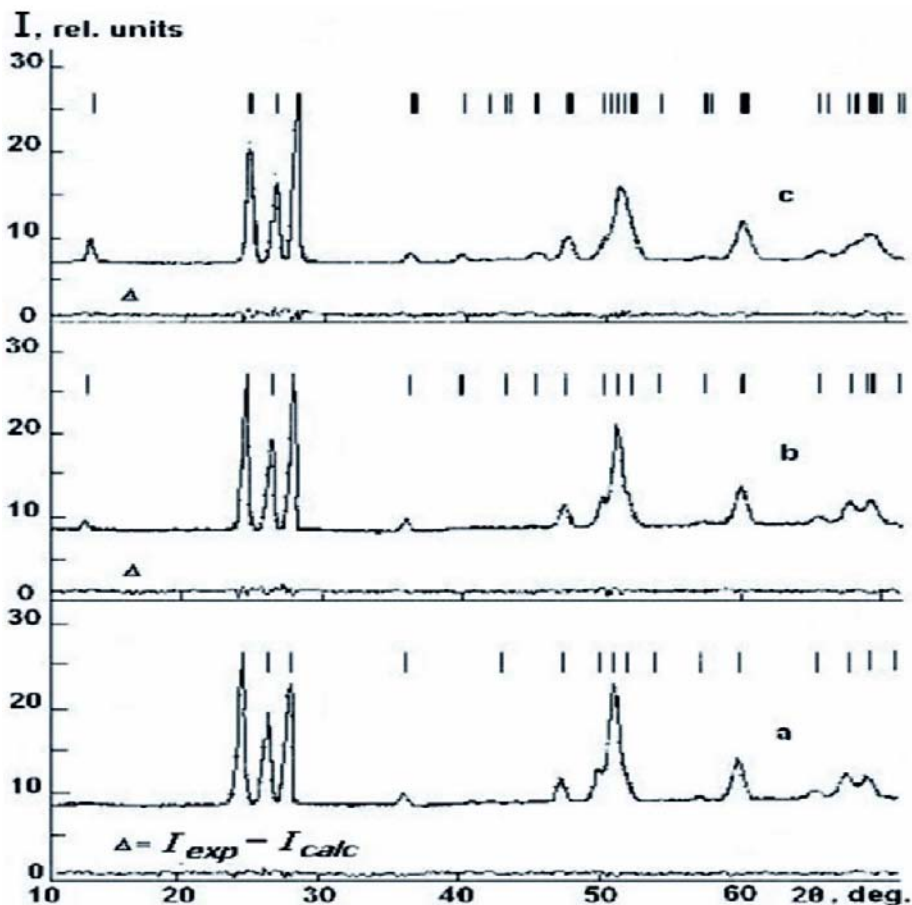


Figure 2. Neutron diffraction patterns of $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) annealed at (a) 1270 K, (b) 1190 K, and (c) 900 K. Dots show measured reflections. The solid curves are simulated patterns.

Based on the neutron diffraction reflections (Fig. 2a) for $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) samples quenched from 1270 K (00l reflections with $l \neq 2n$ are absent; space group $P6_3/\text{mmc}$), the hexagonal structure is the L_3' type, which was possessed by disordered $\text{TiN}_{0.26}\text{H}_{0.15}$ (ss) [2]. Processing the neutron diffraction pattern for the intact solid solution in terms of space group $P6_3/\text{mmc}$ (the α -phase) showed that

samples nitrogen atoms randomly occupy octahedral interstices 2(a), deuterium atoms, both octahedral interstices 2(a) and tetrahedral interstices 4(f). This result supports the structure data reported for disordered $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) [6]. The neutron diffraction patterns of $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) samples quenched from 1190 K (Fig. 2b) or 1160 K after 5 h of exposure display a set of superstructural reflection is the same as in the neutron diffraction pattern of ordered $\text{TiN}_{0.26}\text{H}_{0.15}$ (ss), whose structure is described in terms of space group $P\bar{3}m1$ [7]. Consequently, the crystal structures of ordered $\text{TiN}_{0.26}\text{D}_{0.15}$ and $\text{TiN}_{0.26}\text{H}_{0.15}$ solid solutions belong to the same space group $P\bar{3}m1$ (α' -phase). X-ray powder diffraction show that quenched solid solutions are single-phase with the same unit cell parameters as the disordered solid solution. Two circumstances are noteworthy: firstly, notable superstructure reflections in the $\text{TiN}_{0.26}\text{D}_{0.15}$ neutron diffraction pattern appeared at a higher temperature than in $\text{TiN}_{0.26}\text{H}_{0.15}$ (~ 1190 K against ~ 1020 K [7]); secondly, the neutron diffraction pattern of the $\text{TiN}_{0.26}\text{H}_{0.15}$ (ss) samples quenched from these temperatures showed diffuse reflection (indicative of short-range order [7]), which was not observed in a deuterium solid solution of the same composition. Next, quenches from 1070 and 1020 K strengthen the superstructure reflections in the $\text{TiN}_{0.26}\text{D}_{0.15}$ neutron diffraction pattern, but diffuse reflection does not appear. Note that short-range order in the deuterium solid solution is difficult to study compared to the hydrogen solid solution. The matter is that the diffuse reflection intensity from Ti-N-H and Ti-N-D solid solutions is proportional to the squared difference between the nuclear neutron scattering amplitudes for nitrogen and hydrogen: $I \sim (b_N - b_H)^2$ [8, 9]. It is clear from this that, for $b_N = 0.94 \times 10^{-4}$ Å [10], the substitution of the deuterium nuclear neutron scattering amplitude for the hydrogen nuclear neutron scattering amplitude appreciably decreases the $(b_N - b_H)^2$ value and, accordingly, reduces the diffuse reflection intensity from Ti-N-D solid solution.

An analysis of the reflection intensities in the neutron diffraction pattern for the $\text{TiN}_{0.26}\text{D}_{0.15}$ sample quenched from 1190 K shows that good agreement between the measured and calculated peak intensities (Fig. 2b) and the lowest $R_{\text{Br}} = 5$ % are achievable for the following atom arrangement in terms of space group $P\bar{3}m1$: two titanium atoms occupy the 2(d) positions with coordinates $1/3, 2/3, z_{\text{Ti}}$ and $2/3, 1/3, z_{\text{Ti}}$ ($z_{\text{Ti}} = 0.248 \pm 0.002$); 67 % of the nitrogen atoms occupy octahedral positions 1(a) with coordinates 0,0,0, and 33 % of them occupy octahedral position 1(b) 0,0,1/2; 50 % of the deuterium atoms are located in tetrahedral position 2(d) with a variable parameter $z_D = 0.603 \pm 0.006$ and 50 % of them in the octahedral position 1(a) and 1(b). Therefore, the structure model is an alternation of layers built of metal atoms and of two types of octahedra and tetrahedra. Note that the tetrahedral positions 2(d) with $z_D = 0.128$ lying near the nitrogen plane remain vacant. For comparison, when deuterium atoms were distributed only over two types of tetrahedra, $R_{\text{Br}} < 14$ % was unachievable. The experimentally derived extent of long-range order [11] in the nitrogen sublattice $\eta_{\text{exp}}^{\text{N}} = 0.17$ is one-third the maximum expectation value $\eta_{\text{max}}^{\text{N}} = 0.52$.

TABLE 1. Structural parameters of $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) samples annealed at 1020 K for 24 h (space group $\bar{P}3m1$)

Atom	Position	x/a	y/a	z/a*	n
Ti	2d	1/3	2/3	0.25 ₂	2.000
N1	1a	0	0	0	0.340±0,007
N2	1b	0	0	1/2	0.170±0,003
D1	2d	1/3	2/3	0.600±0,003	0.160±0,001
D2	1b	0	0	1/2	0.130±0,009
R, %	$R_p = 1.6; R_{wp} = 2.3; R_{exp} = 0.8; R_{Br} = 4.5; R_F = 4.7$				
B, Å ²	$B_{Ti} = 0.6 \pm 0.1; B_N = 0.2 \pm 0.1;$ $B_D = 0.8 \pm 0.4$				

B stands for the isotopic thermal factor, *q* for the site occupancy factor, and *R* for the residuals. ^a $x_i/a_i \times 10^4$.

To achieve the maximum ordering, thermal processing was continued. Processing the neutron diffraction pattern from the same sample after annealing it at 1020 K for 5 h increased η to 0.23. This means that the 1(a) site occupancy for nitrogen atoms and the 2(d) site occupancy for deuterium atoms increase with temperature reduction. The superstructure neutron diffraction reflections gain in intensity, especially the 001 superstructure reflection. No attendant changes are observed in the X-ray diffraction patterns. To equilibrate a $\text{TiN}_{0.26}\text{D}_{0.15}$ sample at 1020 K, it was annealed for 24 h. The extent of nitrogen long-range order increased to $\eta_{exp}^N = 0.36$; 57 % of the deuterium atoms occupy tetrahedral intensities 2 (d) and 43 % reside in octahedral 1(b) (Table 1). Locating the deuterium atoms in octahedral positions 1(a) caused most nitrogen atoms to transfer to octahedral 1(b). This is unambiguous evidence that some deuterium atoms remain in the octahedra unoccupied by nitrogen atoms. This character of deuterium distribution differs from hydrogen distribution in $\text{TiN}_{0.26}\text{H}_{0.15}$: in the latter, hydrogen atoms at the initial ordering stage occupy two types of tetrahedra [7,12]. Worth noting is the value of the deuterium free parameter z_D in ordered $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss). In disordered $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss), z_D (equal to 0.635) was larger than for the center of the tetrahedron ($z_{t.c.} = 0.628$) [7]; in the ordered solid solution, $z_D < z_{t.c.}$ (Table 1). Consequently, an alteration in the character of interstitial nitrogen distribution changes the sign of the displacement of deuterium atoms from the center of the tetrahedron. However, z_{Ti} , the displacement of metal atoms along the *c* axis, coincides (to the experimental error) with the value of the free parameter for an ideal hcp lattice ($z_{id} = 1/4$), as opposed to $\text{TiN}_{0.26}\text{H}_{0.15}$ (for which $z_{Ti} = 0.243$ [7]). The following questions arise. What is the character of nonmetal distribution in $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) when the annealing temperature decreases further? Will it be complete ordering or will this solid solution demix into a pair of phases as $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) did? To find answers to these questions, we studied the effect of subsequent low-temperature anneals on the structure of ordered $\text{Ti}_2\text{N}_{0.52}\text{D}_{0.30}$ (ss) (the α' -phase).

First, partially ordered $\text{Ti}_2\text{N}_{0.52}\text{D}_{0.30}$ (ss), prepared by annealing at 1190 K and quenched, was annealed at a lower temperature (900 K) for 24 h. This thermal processing conserved the extant neutron diffraction peaks, but increased the half-width of structure reflection; the half-width of superstructural reflections remained unchanged (Fig. 2c.). At the same time, because of high resolution, the X-ray diffraction peaks, but the 00l peak, undergo clear-cut splitting (Fig. 3). The character of splitting was identical toothed in the monoclinic γ -phase with the structure of anti-AuTe₂, which was observed in $\text{TiN}_{0.32}\text{H}_{0.19}$ and $\text{TiN}_{0.40}\text{H}_{0.21}$ (ss) [13]. Both the X-ray powder diffraction pattern and the neutron diffraction pattern

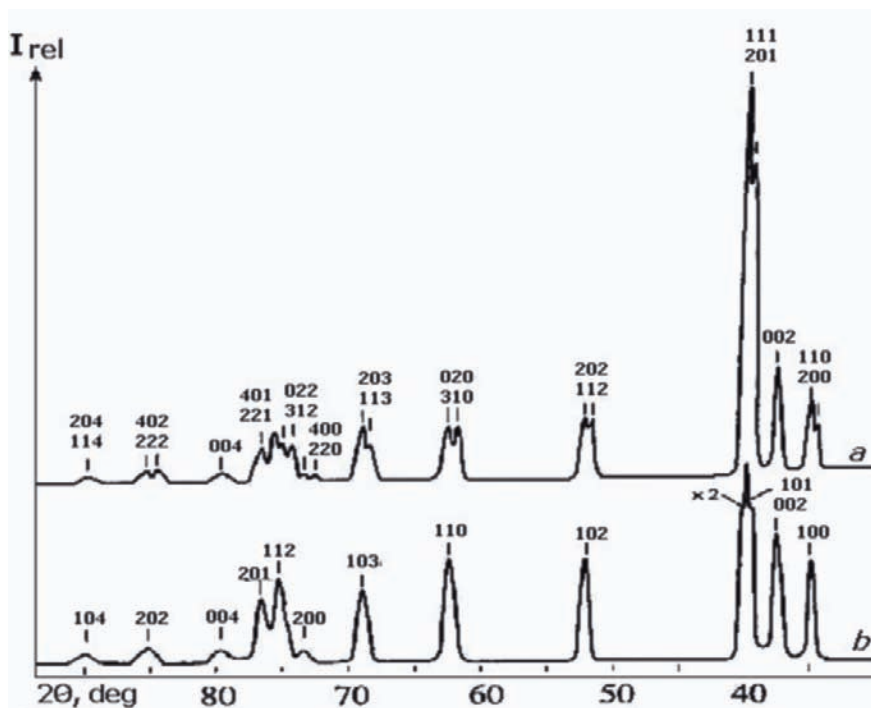


Figure 3. X-ray diffraction patterns for $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss) samples annealed at (a) 1270 K and (b) 900 K. Above peaks Miller indexes of the reflecting planes are indicated.

are indexed in terms of a monoclinic cell with the parameters $a \approx \sqrt{3} a_0$, $b \approx a_0$, $c \approx c_0$, $\beta \approx 89.73^\circ$, where a_0 and c_0 are the parameters of the starting hexagonal cell. Good agreement between the observed and calculated peak intensities (Fig. 2c) and the least residuals (Table 2) were achieved in terms of space group $C2/m$ for the following arrangement of interstitial atoms: nitrogen atoms occupy one type of octahedral positions 2(a) of the two; 73 % of the deuterium atoms occupy tetrahedral position 4(i), and 27 % of them octahedral, positions 2 (c). The c coordinate of metal atoms remains ideal $z_{\text{id}} = 1/4$ to within the calculation error. Along the x axis, metal and deuterium atoms are displaced in opposite from the

ideal position: $x_{id} = 1/3$. Locating nitrogen and deuterium atoms in other positions substantially deteriorates the model convergence. Note that, in the monoclinic phase, the character of atomic ordering remains the same as in the hexagonal phase. Consequently, the observed transition is a result of the action of thermoelastic stress on the ordered phase and is due to the host lattice distortion. Thus, the ordered monoclinic γ -monophase is observed, together with disordered α - and ordered α' -hexagonal phase, in $\text{TiN}_{0.26}\text{D}_{0.15}$ (ss).

TABLE 2. Structural parameters of the γ - $\text{Ti}_2\text{N}_{0.52}\text{D}_{0.30}$ (space group C2/m)

Atom	Position	x/a	$\Delta x/a$	y/b	z/c^a	$\Delta z/c$	q
Ti	4(<i>i</i>)	0.317	0.002	0	0.247	0.002	4.000
N	2(<i>a</i>)	0		0	0		1.040
D(1)	4(<i>i</i>)	0.361	0.007	0	0.609	0.004	0.440± 006
D(2)	2(<i>c</i>)	0		0	½		0.160± 006
$a = 5.147 \pm 0.002 \text{ \AA}; b = 2.997 \pm 0.001 \text{ \AA}; c = 4.810 \pm 0.001 \text{ \AA}; \beta = 89.69^\circ \pm 0.004;$ $B_\Sigma = 0.26 \text{ \AA}^2; R_p = 1.6; R_{wp} = 2.3; R_{exp} = 0.8; R_{Br} = 4.5; R_F = 4.7 \%$							

B_Σ is the effective thermal factor.

Annealing at 740 K for 48 h does not lead to nonmetal ordering in $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ solid solutions. Ordering occurs only after 186 h of annealing. The X-ray diffraction pattern of this samples annealed at 740 K does not show signs of exsolution even after 186 h of exposure. The neutron diffraction pattern recorded in 10' scan steps shows superstructure reflection, indicating nonmetal ordering in host interstices. However, these reflections are significantly broader than those in the neutron diffraction patterns of the samples quenched from high temperatures. Recording a neutron diffraction pattern with smaller scan steps of 5' revealed split superstructure reflection (Fig. 4). Splitting of each of these reflections into a triplet of symmetrically arranged reflections is evidence that periodic, ordered antiphase domain (APhD) structure is formed in the solid solution below the exsolution point (at $T < T_d$) [14]. The fact is worth noting that splitting is experienced by both 001 superstructure reflection and the 111 reflection (which is also a superstructure reflection). Therefore, domain ordering in the solid solution has no layered character, that is, it occurs in various directions (rather than in one). The distance between the satellites of the super-structure reflection was used to determine the period of an ordered APhD structure [15]. The period of the APhD structure determined from the 003 reflection is ten times c . The absence of APhD ordering in the samples annealed at high temperatures can be understood as the formation of large and randomly oriented APhDs at these temperatures. At temperatures far lower than T_d (at 740 K), fine and oriented APhDs are slowly formed. Indeed, values of 60, 240, and 420 Å were found from the Selyakov-Scherrer relationship [16] for the same exposure time (24 h) and the temperature of 800, 890 and 920 K, respectively. Because APhD ordering is observed below 800 K, the size of ordered domains may be set smaller than 60 Å. The subsequent low-temperature (740 K)

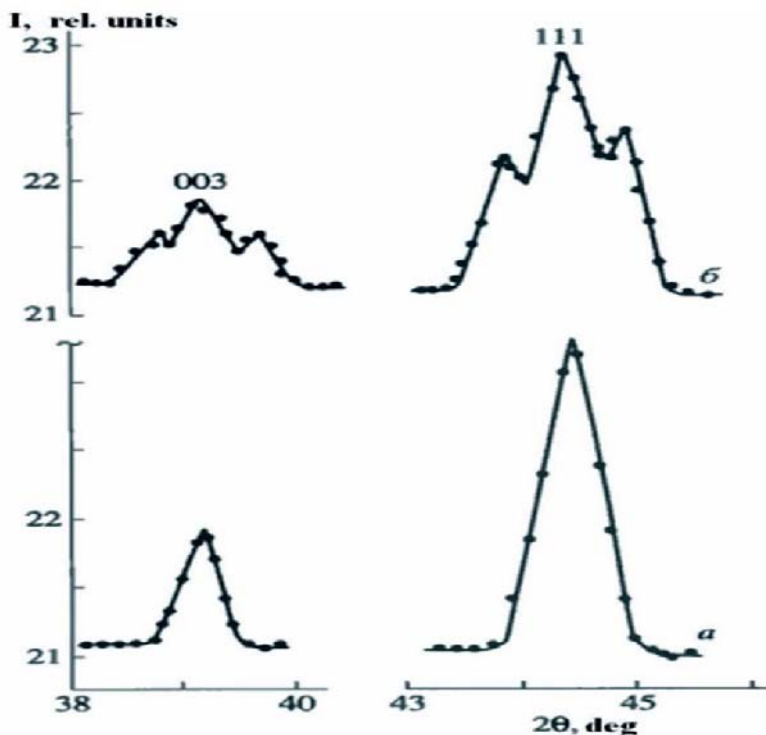


Figure 4. Superstructure neutron diffraction reflections from $\text{TiN}_{0.26}\text{H}_{0.15}$ (ss) after annealed for 186 h at (a) 890 K and (b) 740 K.

annealing of the solid solution that has been ordered at relatively high temperatures (at $T \geq T_d$) does not cause APhD ordering. It seems that a slow growth of fine APhDs is required for ordered APhDs to appear, which in turn requires annealing at temperatures far lower than T_d . The absence of demixing can be interpreted by the slow kinetics of the process conditioned by a limited diffusion mobility of atoms.

Figure 5 shows the neutron diffraction pattern of $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ received by quenching from temperature of 1270 K. According to neutron data, $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ (ss) has a hexagonal ordered structure: space group $P\bar{3}m1$, where the nitrogen atoms occupy octahedral position 1(a), the hydrogen atoms are located in tetrahedral positions 2 (d) $z = 0.754$, 80 % of the deuterium atoms - tetrahedral positions 2 (d) with $z = 0.636$ and 20 % of them in the octahedral position 1(b). As against $\text{TiN}_{0.26}\text{H}_{0.15}$ (Fig. 1a) and $\text{TiN}_{0.26}\text{D}_{0.15}$ (Fig. 2a) solid solutions, $\text{TiN}_{0.26}\text{D}_{0.08}\text{H}_{0.08}$ (ss) with the high-temperature state has a ordered structure (Fig. 5). Hence, the transition temperature of the order-disorder in $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ is higher than in $\text{TiN}_{0.26}\text{H}_{0.15}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ solid solutions.

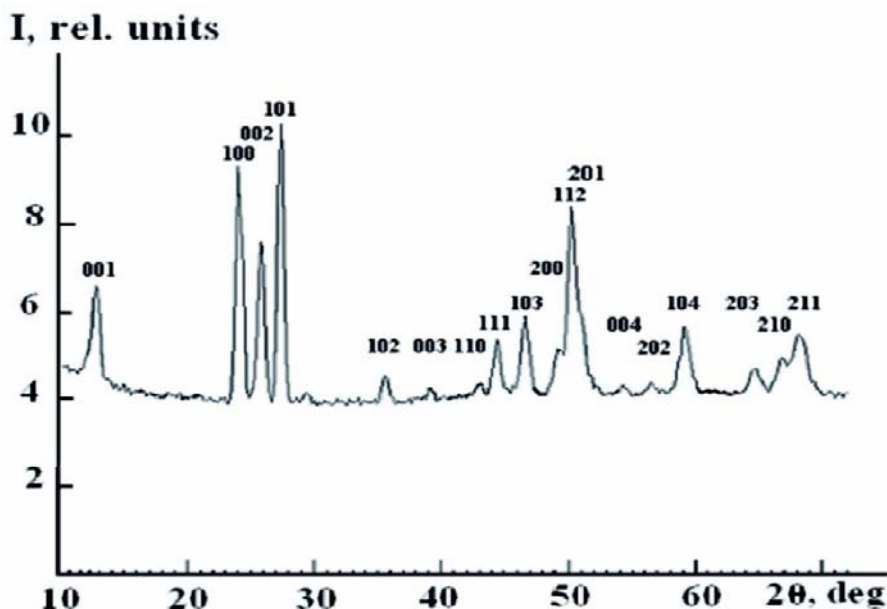


Figure 5. Neutron diffraction patterns of $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ (ss) quenched from 1270 K.

Conclusions

Neutron diffraction study of the solid solutions $\text{TiN}_{0.26}\text{D}_{0.15}$, $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ and comparison the results with results of investigation of the $\text{TiN}_{0.26}\text{H}_{0.15}$ allowed to reveal isotopic effect, revealing in following.

1. Nitrogen ordering in $\text{TiN}_{0.26}\text{D}_{0.15}$, $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ in terms space group $P\bar{3}m1$ starts at higher temperatures (~ 1270 K and ~ 1170 K, accordingly) than in $\text{TiN}_{0.26}\text{H}_{0.15}$ (~ 1020 K).
2. Unlike $\text{TiN}_{0.26}\text{H}_{0.15}$, in $\text{TiN}_{0.26}\text{D}_{0.15}$, the appearance of superstructural reflections in the neutron diffraction patterns is not preceded by diffuse scattering.
3. The low-nitrogen homogeneity boundary of the monoclinic ordering phase with space group $C2/m$ in the Ti-N-D system lies at lower nitrogen concentrations than in the Ti-N-H system; the $\text{TiN}_{0.26}\text{D}_{0.15}$ sample is the single monoclinic phase at temperature of 900 K.
4. Hydrogen atoms in ordered $\text{TiN}_{0.26}\text{H}_{0.15}$ reside only in tetrahedral positions; in ordered $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ and $\text{TiN}_{0.26}\text{D}_{0.15}$ some deuterium atoms also occupy the octahedral positions unoccupied by nitrogen atoms.

The higher onset temperature of ordering in the Ti-N-D system than in the Ti-N-H system can be interpreted as follows. In highly imperfect solid solutions, an essential role is played by strain, long-range interactions [17]. It can be therefore suggested that the replacement of H by D atoms in the solid solution changes the lattice strain field and, in all probability, enhances the stability of the ordered state

of the solid solution. The disordering temperature becomes higher in association. The results of study $\text{TiN}_{0.26}\text{H}_{0.075}\text{D}_{0.075}$ show that heterogeneity lattice field of the interstitial atoms else intensifies the strain interaction.

As regards the location of part of the D atoms in $(0,0,1/2)$ octahedral of ordered α' - and γ -phases, it may be presumed that the blocking effect caused by repulsion forces between a nitrogen atom N in a octahedron $(0,0,0)$ and a deuterium atom D in a tetrahedral is stronger than between N and H atoms. As a result, part of the D arrears at longer distances (in $1(b)$).

Acknowledgements

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SYNTHESIS, PROPERTIES, AND ASSIMILATION METHODS OF ALUMINIUM HYDRIDE

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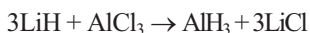
Abstract. We have discovered a new source of aluminum hydride – conversion of tetrahydroaluminates under influence of halogenous alkyls. We have proposed the chlorobenzene method of synthesis of AlH_3 , which excludes adhesion and ensure high quality of the product with respect to its purity, thermal stability, habits of crystals (round shape), and granulometric composition. We determined capability of benzyl chloride to fix AlH_4^- groups by the way of complexes formation. This allows increasing efficient concentration of AlH_3 solutions and their productivity.

We have carried out "direct" crystallization of aluminum hydride in one stage using interaction of binary metal hydride with aluminum chloride in the medium of ether-toluene at 60-100°C and using solvent distillation. In the reaction of LiH with AlCl_3 , we achieved output of pure crystal AlH_3 of hexagonal modification, which was close to quantitative.

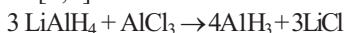
We have discovered the assimilation methods of aluminum hydride in carrying out of solid-phase chemical reactions.

Keywords: aluminum hydride, tetrahydroaluminates of metals, synthesis, properties, benzyl chloride

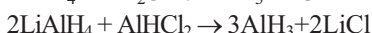
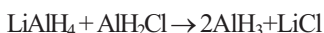
Aluminum hydride is an intermediate product of synthesis of lithium tetrahydroaluminate



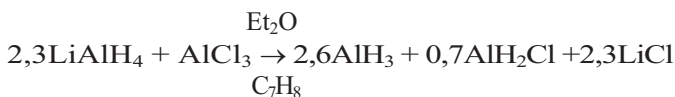
and is synthesized during interaction of lithium tetrahydroaluminate with aluminum chloride [1,2]



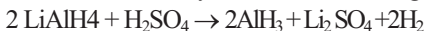
Depending on quantitative ratio of chemical agents, this reaction may also result with synthesis of chloralanes AlH_2Cl or AlHCl_2 . Chloralane interacts with lithium tetrahydroaluminate in ether with formation of aluminum hydride [3]:



In «chloralane» method, we use surplus of AlCl_3 up to 30% and get ether-toluene solution of etherates of aluminum hydride and monochloralane [4, 5],



We have also synthesized aluminum hydride by interaction of LiAlH_4 , with H_2SO_4 in the medium of tetrahydrofuran according to reaction [6]:

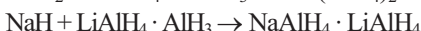
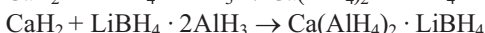
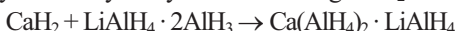


In chlorine-silane method of synthesis of aluminum hydride [6]



along with target product is synthesized silane, which is very valuable for synthesis of semiconductor silicon.

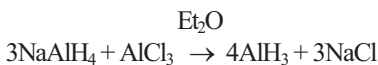
Aluminum hydride may be synthesized using CaH_2 and NaH [7]:



Further process with AlCl_3 proceeds as usual exchange reaction:



During synthesis of AlH_3 using NaAlH_4 , we achieved decrease of chlorine influence on the process, taking into account practically insolubility of sodium chloride in ether:



We have developed several new methods of synthesis of AlH_3 in the present work. Hydrogen chloride, being very strong proton-containing acid, especially in the medium of non-solvating solvent, easily displace AlH_3 from tetrahydroaluminate's molecule. During this process aluminum hydride displays properties of Luis weak acid [8-10].

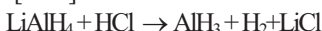


Figure 1 shows kinetic curved lines of AlH_3 decomposition. As can be seen from figure, the most stable AlH_3 were synthesized during interaction of LiAlH_4 solution with solutions of HCl + toluene (samples 10, 22)

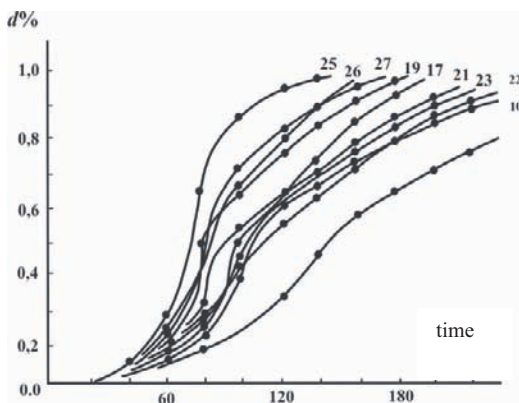


Figure 1. Kinetic curved lines of decomposition of aluminum hydride's samples at 130°C, which were synthesized using LiAlH_4 and HCl .

We proposed synthesis method of AlH_3 by the way of interaction with halogenous alkyls and aralkylhalogenids (tables 1 and 2) [11, 12].

From all reactions of hydrogenolysis for synthesis of AlH_3 we chose interaction reaction of LiAlH_4 with benzyl chloride [11, 12]

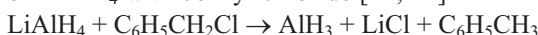


Table 1 Synthesis of aluminum hydride by the way of interaction of LiAlH_4 with RCl in the medium of ether-toluene

No. of experiment	Chlorine-derivatives of hydrocarbons	Taken, g/moles		Mole ratio	Period of synthesis, in minutes	Temperature of synthesis, °C	Output % AlH_3	Type of AlH_3 crystals	Composition of product		
		LiAlH_4	RHal						Al weight %	H weight %	Cl weight %
1	Allyl Chloride	6,35 0,167 0	13,25 0,173 0	1:0,97	40	30-40	52,8	Grey pieces	82,0	-	-
2	Allyl Chloride	6,45 0,170 0	13,40 0,175 0	1:0,98	40	35-45	62,7	Grey pieces	84,2	-	-
3	Butyl Chloride	6,40 0,168 0	13,80 0,149 0	1:0,90	40	40-50	-	Grey pieces	-	-	-
4	Butyl Chloride	6,50 0,177 0	13,90 0,15	1:0,92	40	40-60	62,1	Pins, agglomerates	78,6	-	-
5	Octyl Chloride	7,97 0,21	30,10 0,202	1:0,97	40	40-50	80,5	Granules	87,8	9,78	traces
6	Octyl Chloride	7,80 0,206	30,20 0,2025	1:0,98	45	40-60	85,2	Pins, stars	89,2	9,80	no
7	Benzyl Chloride	6,30 0,166	20,0 0,158	1:0,88	30	40-60	70,8	Pins, granules	89,8	9,71	no
8	Benzyl Chloride	6,45 0,17	20,95 0,165	1:0,94	30	40-60	83,0	granules	89,6	9,86	no

Table 2 The conditions and results of interaction tests of $\text{M}(\text{AlH}_4)_2$ with RHal .

No. of test	Haloid-derivatives of hydrocarbons	Amount of tetrahydrofuran solution	Concentration of solution $\text{M}(\text{AlH}_4)_2$, g/l	Mole ratio		Period of synthesis in minutes	Temperature of synthesis, °C	Solution analysis		Atomic ratio Al:H
				$\text{Ca}(\text{AlH}_4)_2$	$\text{Sr}(\text{AlH}_4)_2$			Al g/l	H, g/l	
1	Allyl Chloride	70	13,3	1:2,0	-	60	30	6,94	0,75	1:2,90
2	Butyl Chloride	100	21,5	-	1:2,0	50	40	7,69	0,84	1:2,94
3	Benzyl Chloride	70	13,3	1:1,9	-	90	60	6,81	0,72	1:2,86
4	Butyl Bromide	100	21,5	-	1:2,0	20	30	7,58	0,82	1:2,91
5	Hexyl Bromide	70	13,3	1:2,1	-	30	40	6,89	0,72	1:2,82
6	Benzyl Chloride	100	21,5	-	1:2,0	120	50	7,86	0,87	1:2,98
7	Butyl Chloride	120	15,9	1:7,9	-	60	60	8,29	0,90	1:2,95
8	Benzyl Chloride	150	25,6	-	1:8,0	90	60	9,1	0,98	1:2,90

1. Physical and chemical properties of AlH_3

Figure 2 shows the thermogram of AlH_3 of hexagonal modification. As may be seen from the figure, AlH_3 decomposes at 170°C [12-15]. Conversion of rhombic modification into hexagonal takes place during short-time heating of sample and is fixed in thermogram by exoenergetic effect in the temperatures interval $110\text{-}120^\circ\text{C}$. Bridge, deformative fluctuations of Al-H appeared on infrared spectra of aluminum hydride. Bridge fluctuations for hexagonal modification are fixed in the frequency range 1819 cm^{-1} and 1640 cm^{-1} , deformative fluctuations for hexagonal modification are fixed in the frequency range 864 cm^{-1} , 741 cm^{-1} , and 667 cm^{-1} [14, 15, 11].

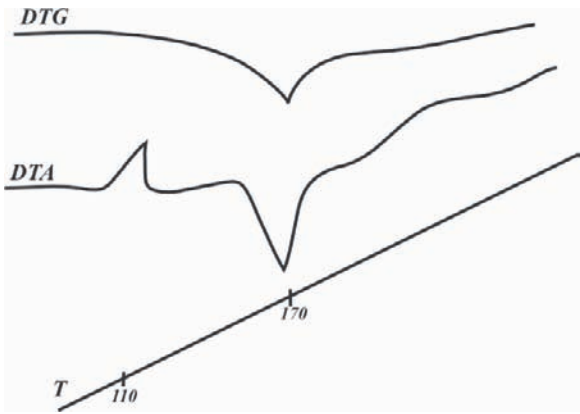


Figure 2. AlH_3 Thermogram.

Table 3 shows crystal modifications of aluminum hydride. Standard free Gibbs energy AlH_3 synthesis has positive value (Table 4).

Table 3 Crystal modification of AlH_3

	Parameters of elementary cell			Z	D g/sm^3	Literature
	a	b	c			
Cubic (γ)	9,04			16	1,22	[16]
Cubic	8,38				1,52	[16,17]
Hexagonal (α)	4,45		11,81	6	1,47	[16]
Hexagonal	2,9		4,55			[18]
Hexagonal (II)	8,04		12,58			[15]
Hexagonal (III)	6,56		10,61			[15]
Rhombic	3,18		1,56			[16]
Rhombic	5,32	7,31	5,82	6	1,31	[16]
Rhombic	6,91	5,02	6,73	6	1,26	[14]
Rhombic	6,62	6,48	5,62	6	1,24	

**Table 4 Thermodynamic properties of α - and β -forms of
aluminum hydride, kilocalorie/mole**

Crystal modification	ΔG_f^0	$-\Delta H_f^0$	$\Delta H_{\text{different.}}$	E of decomposition activity
Hexagonal (α)	11[19]	27,3 [20,19] 2,03 [21] 2,44 2,70	2,96 [18] 3,22 0,68	24-27
Rhombic (β)	12[21]	0,59		

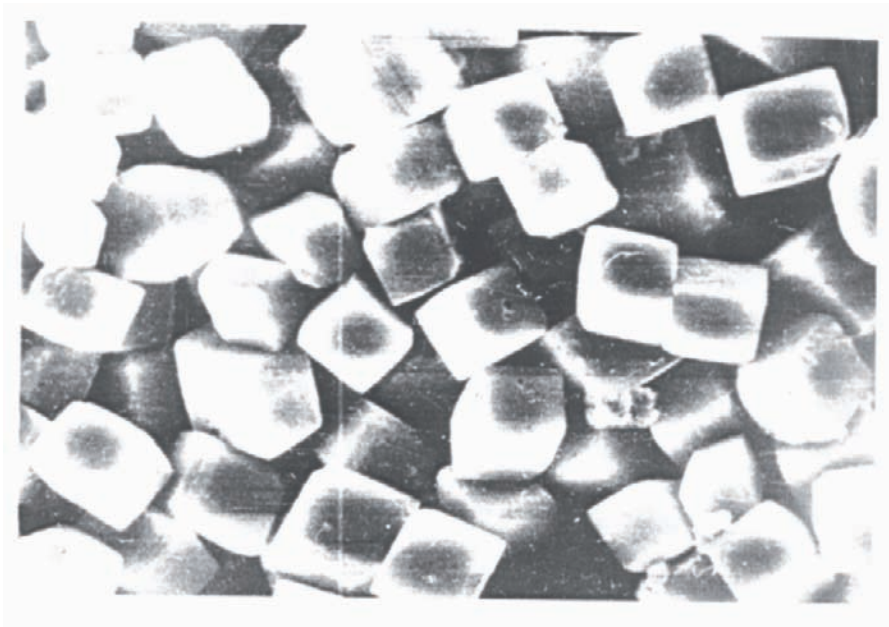


Figure 3. Appearance of aluminum hydride crystals, synthesized by Benzyl Chloride.

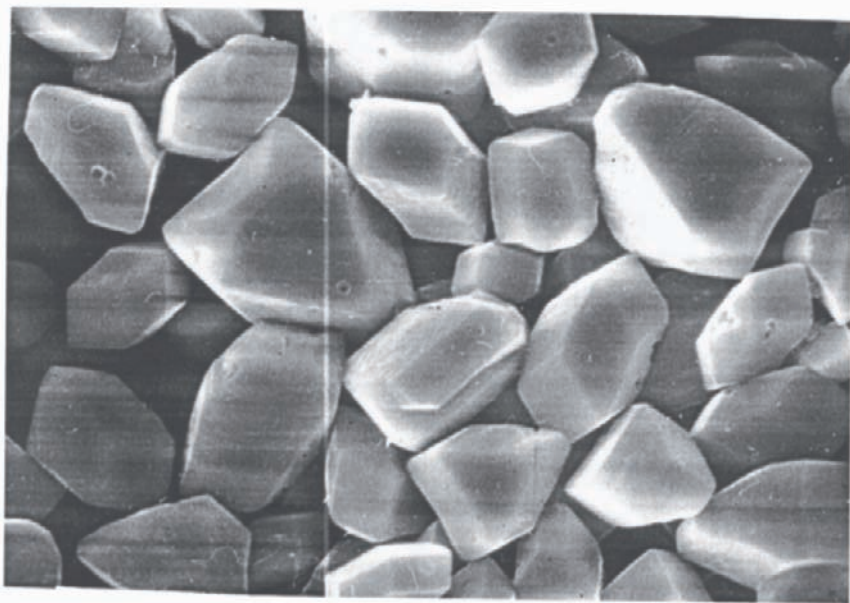
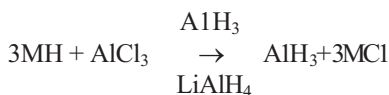
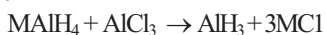


Figure 4. Appearance of aluminum hydride crystals, synthesized by "direct" method.

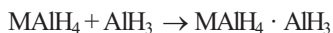
We have developed "direct" method of crystallization of aluminum hydride using interaction of lithium hydride with aluminum chloride. We have determined that full chloride exchange at interaction of metal hydride with aluminum chloride



may be achieved only in conditions of behavior of direct and reverse reactions with formulae



and



at separate addition of chemical agents MH and AlCl_3 with exclusion of their direct contact [11,13].

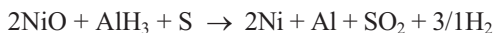
In the first stage of «alan» method we carried out interaction of binary hydrides of alkaline, alkaline-earth metals and aluminum as etherate $\text{AlH}_3 \cdot n\text{Et}_2\text{O}$ (or AlH_3) in mole ratio $\text{MH}_2 : \text{AlH}_3 = 1:2$ in the medium of ether with intensive mixture and operation mode with surplus of AlH_3 :



In the second stage we carried out interaction of synthesized hydride aluminates with aluminum chloride in mole ratio $\text{M}(\text{AlH}_4)_2 : \text{AlCl}_3 = 3:2$ in the medium of ether or ether-toluene 1:1÷2,5 and synthesized aluminum hydride



In this work, we also have considered assimilation of AlH_3 in carrying out of solid-phase chemical reactions. We have considered interactions in the system



with the purpose of synthesis of magnetic powders of nickel by plazmochemical method, (where ΣH – hydrogen atoms' stream in plasmatron) [22].

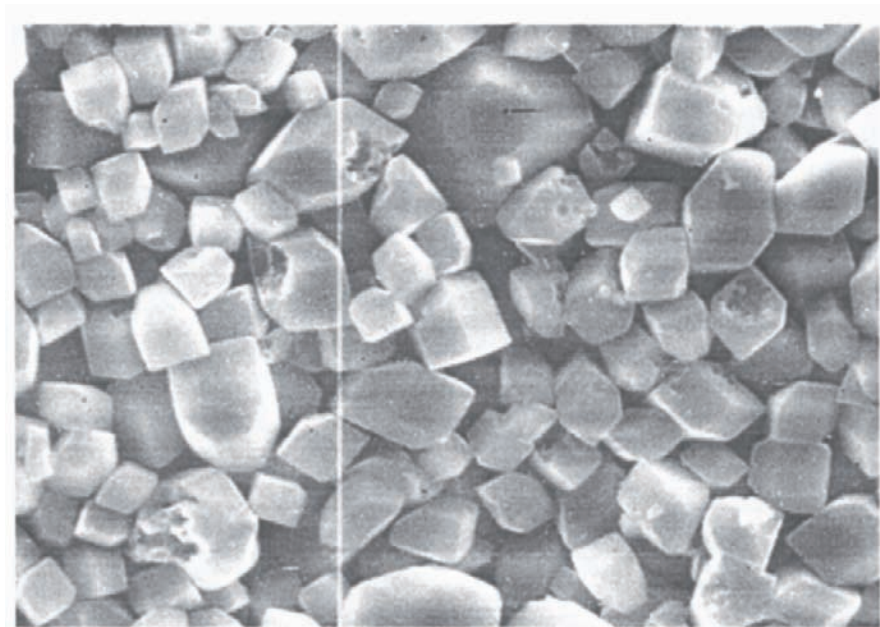


Figure 5. Appearance of aluminum hydride crystals. ("Alan" method).

In the presence of AlH_3 we have considered synthesis reaction of cadmium iodide at bombardment of mixture $\text{CdS} + \text{J}$ [23] with hydrogen atoms. We have investigated catalytic properties of AlH_3 at opening of different minerals [24].

Thus, we have discovered a new source of aluminum hydride - conversion of tetrahydroaluminates under influence of halogenous alkyls. We have proposed the chlorinebenzene method of synthesis of AlH_3 , which excludes adhesion and ensure high quality of the product with respect to its purity, thermal stability, habits of crystals (round shape), and granulometric composition. We have determined capability of benzyl chloride to fix AlH_4^- - groups by the way of complexes formation. This allows increasing efficient concentration of AlH_3 solutions and their productivity.

We have carried out "direct" crystallization of aluminum hydride in one stage using interaction of binary metal hydride with aluminum chloride in the medium of ether-toluene at 60-100°C and using solvent distillation. In the reaction of LiH with AlCl_3 we achieved output of pure crystal AlH_3 of hexagonal modification, which was close to quantitative.

We discovered the assimilation methods of aluminum hydride in carrying out of solid-phase chemical reactions.

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INFLUENCE OF HYDROGEN ORDERING ON THE PROTON SPIN-LATTICE RELAXATION TIME IN LANTHANUM SUPERSTOICHIOMETRIC DIHYDRIDES LaH_{2+c}

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Abstract. The influence of hydrogen ordering processes on the temperature dependence of the proton spin-lattice relaxation time $T_1(T)$ in lanthanum hydrides is estimated. It is shown that on taking into account the dipole-dipole interaction of hydrogen and metal atoms, and the interaction of hydrogen atoms with conduction electrons, an excellent description of the experimental $T_1(T)$ dependence can be obtained. It is shown as well that spatial redistribution of ordering octa-hydrogen atoms induces a negligibly small changes in the calculated $T_1(T)$ dependence, as the major part of the dipole-dipole interaction is related with the unchanged totalities of tetra-hydrogens and metal atoms.

Keywords: Metal hydrides, phase transitions, hydrogen ordering; NMR, spin-lattice relaxation time.

1. Introduction

We consider the β -phase of lanthanum hydrides LaH_{2+c} , where N metal atoms form a fcc lattice, $2N$ tetrahedral interstices are occupied by $2N$ hydrogen atoms (denoted as H_T -atoms), and on the set of N octahedral interstices are distributed the additional cN hydrogen atoms (denoted as H_O -atoms). The subsystem of H_O -atoms undergoes disorder-order and order-order transitions [1]. Correspondingly the high-temperature disordered state at temperature T_{tr1} is replaced by the “ordered state I” and at temperature T_{tr2} by the “ordered state II”. Phase diagram of the ordering subsystem is presented in Fig. 1 [2]. *The problem under consideration.* In articles [3] we had analytically considered the possible modifications of the temperature dependence of proton spin-lattice relaxation time T_1 in metal hydrides caused by the hydrogen ordering processes. In [4] were given the results of precise NMR measurements of lanthanum hydrides. The aim of the present report can be formulated as an attempt of the numerical calculations of $T_1(T)$ dependence in lanthanum hydride on comparing with the experimental results [4].

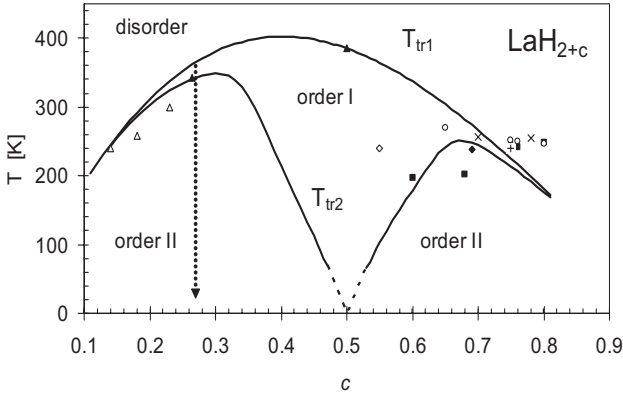


Figure 1. (c, T) phase diagram of LaH_{2+c} system [2].

2. Proton spin-lattice relaxation time in hydrides

In the external constant magnetic field H_0 the nuclear magnetic moments of hydrogens μ_I (associated with the nuclear spin $I = 1/2$), and that of metallic atoms μ_S (associated with the nuclear spin S), rotate with the Larmor frequencies $\omega_I = g_I H_0$ and $\omega_S = g_S H_0$, where g_I and g_S are the giromagnetic ratios of corresponding nuclei.

It is well known that total spin-lattice relaxation time T_1 can be written as

$$T_1^{-1} = T_{1d}^{-1} + T_{1e}^{-1} + T_{1p}^{-1}, \quad (1)$$

where T_{1d} is the spin-lattice relaxation caused by dipole-dipole interactions, T_{1e} is that caused by conduction electrons, and T_{1p} – caused by paramagnetic impurities. As we wish to compare our results with the measurements [4] performed on “pure” $\text{LaH}_{2.27}$, we shall assume that $T_{1p}^{-1} = 0$.

For electronic contribution will be used the Korringa relation

$$T_{1e} = K / T, \quad (2)$$

and for the dipole-dipole contribution - the well known expression, written as

$$T_{1d}^{-1} = \tau [J^H(T) \Sigma_j^H + J^M(T) \Sigma_j^M], \quad (3)$$

where $J^H(T)$ and $J^M(T)$ are temperature-dependent factors,

$$J^H(T) = (2/5) C_I \{ [1 + (\omega_I \tau)^2]^{-1} + 4 [1 + (2\omega_I \tau)^2]^{-1} \}, \quad (4a)$$

$$J^M(T) = (2/15) C_S \{ [1 + (1 - (g_I/g_S))^2 (\omega_I \tau)^2]^{-1} + 3 [1 + (2\omega_I \tau)^2]^{-1} + 6 [1 + (1 - (g_I/g_S))^2 (\omega_I \tau)^2]^{-1} \}; \quad (4b)$$

$$C_I = g_I^4 h^2 I(I+1), \quad C_S = g_I^2 g_S^2 h^2 S(S+1). \quad (4c)$$

(g_I , g_S , ω_I , ω_S , I and S were introduced above.)

τ^{-1} is the hydrogen jump frequency,

$$\tau = \tau_0 \exp(E_a / k_B T). \quad (5)$$

and E_a is the hydrogen jump activation energy.

$\Sigma_j^M = \Sigma_j^M(r_j^{-6})$ denotes summation over all metal atoms, and r_j denote the distances between the given interstitial H-atom and all metal lattice sites.

$$\Sigma_j^H = [\Sigma_{jT}^H(r_j^{-6}) + \Sigma_{jO}^H n_j(T)(r_j^{-6})] \quad (6)$$

denotes the sum over all tetrahedral and octahedral interstitial positions. Here r_j are the distances between the position, actually occupied by the “resonant” hydrogen atom, and other interstitial positions.

It is assumed that all tetrahedral interstices are occupied by H_T -atoms with a constant probability $n_H = 1$. Octahedral positions are occupied by H_O -atoms with probabilities depending on the site's number j , $n_j(T) \leq 1$.

In the high-temperature disordered state $n_j(T) = c = \text{const.}$, while in the low-temperature ordered configurations $n_j(T) = n_1(T), n_2(T), n_3(T)$. Generally, $n_1 \neq n_2 \neq n_3$, and particularly, $n_1 > n_2 > n_3$ (see below).

Hydrogen ordering modifies slightly the metal lattice that implies small displacements of metal atoms and H_T -atoms from their ideal geometrical positions, but we neglect this effect and assume that hydrogen ordering changes only the sum $\sum_{jO}^H n_j(T)(r_j^{-6})$.

3. Description of the hydrogen ordering process

The totality of octa-positions in the fcc metal lattice form itself an fcc lattice. In the case of $c < 1$, on the set of N octa-positions are distributed cN H_O -atoms. Experimentally was established that at lowering temperatures on the set of H_O -atoms the ordering processes are developed and superstructures are formed. In [1] it was shown that the experimental superstructures have to be characterized by a pair of order parameters, η_1 and η_2 . Correspondingly, the set of octa-positions can be subdivided into three groups differing by the occupation probabilities. In the disordered state all octa-positions had a similar occupation probability: $n_j = c$. In the ordered configurations the situation is different: $\nu_1 N$ octa-positions have an occupation probability $n_j = n_1$, $\nu_2 N$ positions - an occupation probability $n_j = n_2$, and $\nu_3 N$ positions - an occupation probability $n_j = n_3$. Relations between occupation probabilities and order parameters are as follows [1]:

$$n_1 = c + \eta_1 \gamma + 2 \eta_2 \gamma, \quad n_2 = c + \eta_1 \gamma - 2 \eta_2 \gamma, \quad n_3 = c - \eta_1 \gamma. \quad (7)$$

Restrictions imposed on occupation numbers n_j and octa-position parts ν_i look as:

$$0 \leq n_1, n_2, n_3 \leq 1, \quad \nu_1 + \nu_2 + \nu_3 = 1. \quad (8)$$

Development of the ordering process can be described by the temperature-dependent equilibrium values of order parameters $\eta_1(T)$, $\eta_2(T)$ (see Fig. 2a), by the trajectory of the process on the (η_1, η_2) -plane (Fig. 2b) and by the temperature-dependent occupation probabilities $n_1(T)$, $n_2(T)$, $n_3(T)$ (see Fig. 2c).

Temperature variations of equilibrium order parameters η_1 and η_2 , and equilibrium occupation numbers n_1 , n_2 and n_3 , shown in Figs. 2, are determined following the scheme [1]. All numerical calculations have been performed for $\text{LaH}_{2.27}$ (i.e. for $c = 0.27$), indicated in Fig. 1 by an arrow.

Phase transformations indicated in Figs. 2a – 2c occur at temperatures:

$$T_{tr1} = 365 \text{ K}, \quad T_{tr2} = 343 \text{ K}.$$

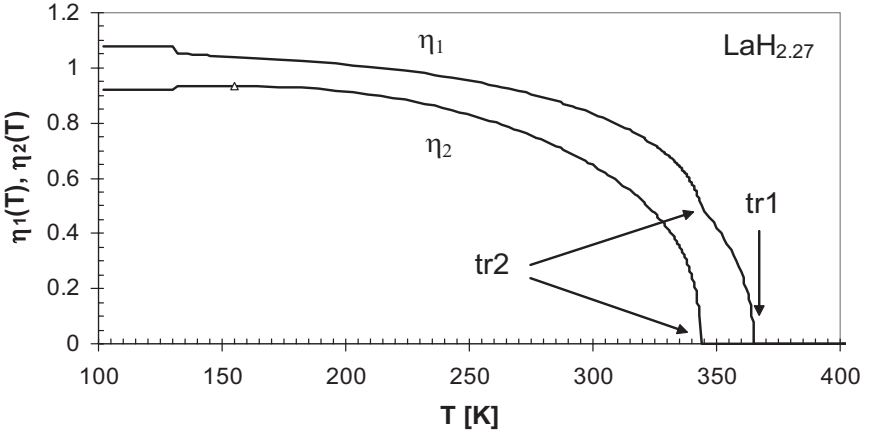


Figure 2a. Temperature dependences of equilibrium order parameters, $\eta_1(T)$, $\eta_2(T)$.

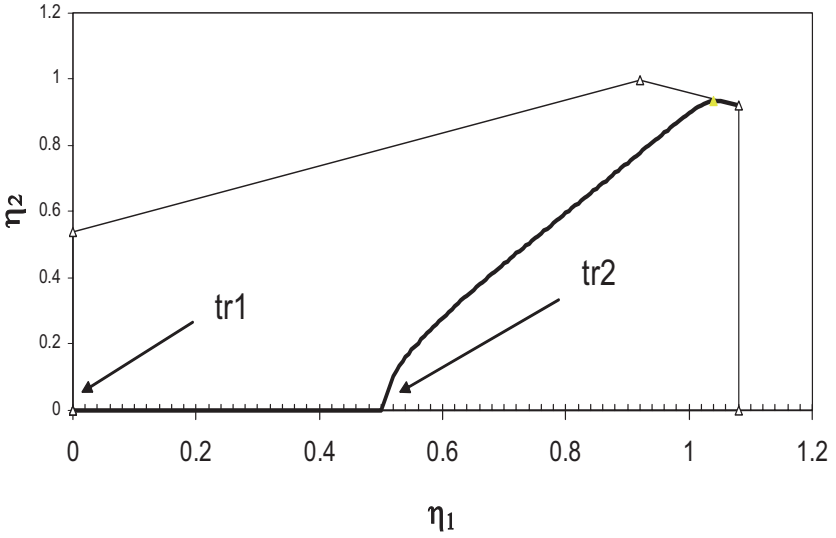


Figure 2b. Equilibrium trajectory of the ordering process in the $\{\eta_1, \eta_2\}$ -plane. $\text{LaH}_{2.27}$.

Below the phase transition point T_{tr1} an equilibrium configuration $\{\eta_1 \neq 0, \eta_2 = 0\}$, or $\{n_1 = n_2 \neq n_3\}$ is formed, while below T_{tr2} in equilibrium will be configurations of the type $\{\eta_1 \neq 0, \eta_2 \neq 0\}$, or $\{n_1 \neq n_2 \neq n_3\}$.

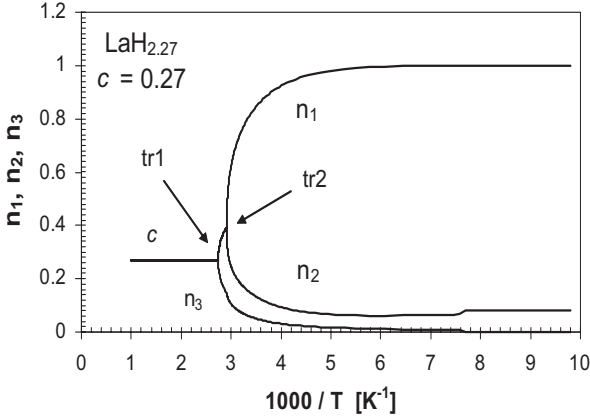


Figure 2c. Temperature dependence of occupation numbers.

4. Results of numerical calculations

Experimental dependence $T_1(T)$ for $\text{LaH}_{2.27}$ [4] is given in Fig. 3.

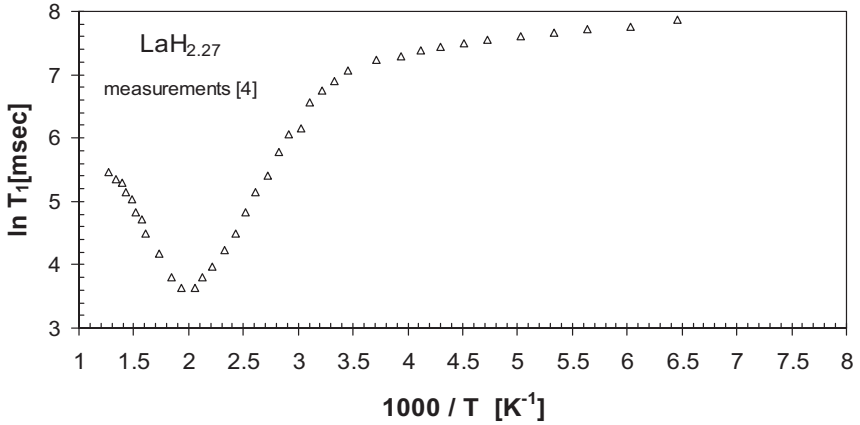


Figure 3. Experimental dependence of the spin-lattice relaxation time in $\text{LaH}_{2.27}$ [4].

Theoretical $T_1(T)$ dependences calculated following expressions (1) – (5), on neglecting the ordering effects and using the values of fitting parameters K , τ_0 and E_a proposed in [4], are given in Fig. 4a. The values of fitting parameters are as follows:

$$K = 410 \text{ sec K}, \quad E_a = 0.35 \text{ eV/atom}, \quad \tau_0^{-1} = 7.4 \times 10^{11} \text{ sec}^{-1}.$$

Figure 4b illustrates the role of hydrogen ordering process. There is given “delta”, the difference in $T_1(T)$ dependences calculated with and without taking into account the ordering effects illustrated by Figs. 2.

$$\text{"delta"} = \{ T_1(T) \}_{\text{ordered}} - \{ T_1(T) \}_{\text{disordered}}.$$

Here $\{T_1(T)\}_{\text{ordered}}$ implies calculation of the sum $[\sum_{jO}^H n_j(T)(r_j^{-6})]$ in (6) using the determined values of equilibrium occupation numbers $n_1(T)$, $n_2(T)$ and $n_3(T)$, while $\{T_1(T)\}_{\text{disordered}}$ implies replacement of the above sum by the expression $[c \sum_{jO}^H (r_j^{-6})]$ at all temperatures. As it can be seen from Fig. 4b the difference "delta" seems to be very small to be registered in the measurements.

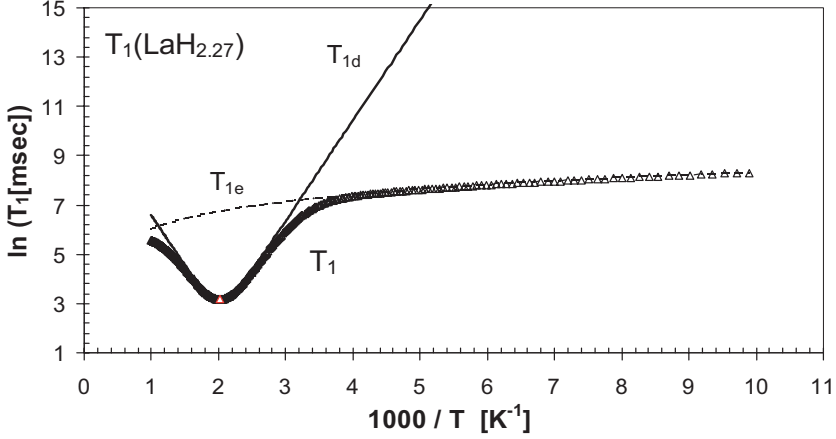


Figure 4a. Electronic part T_{1e} , dipole-dipole part T_{1d} and the total spin-lattice relaxation times T_1 , assuming disordered configuration of H_O -atoms at all temperatures.

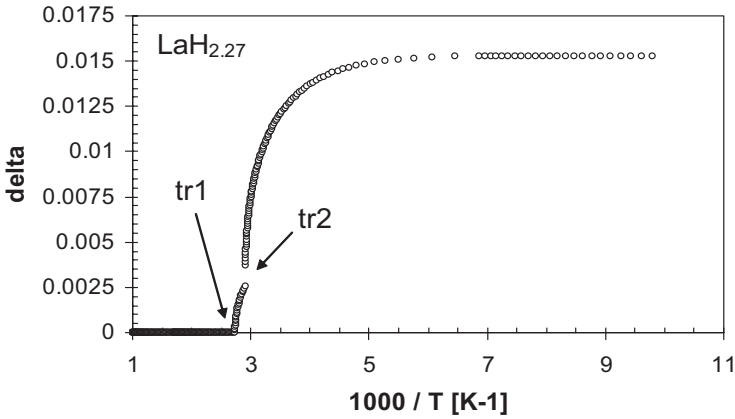


Figure 4b. Difference between the T_1 -values calculated on accounting the ordering process and on neglecting it.

In the given below Fig. 5 we illustrate the possibilities of reproduction of the experimental points (Fig. 3) by a theoretical curve, without taking into account the ordering processes (Fig. 4a). Coming from the negligible difference between the relaxation processes in the ordered and disordered configurations (Fig. 4b), it can

be concluded that experimental points in Fig. 3 can be described by the theoretical curve accounting for the ordering processes similarly well.

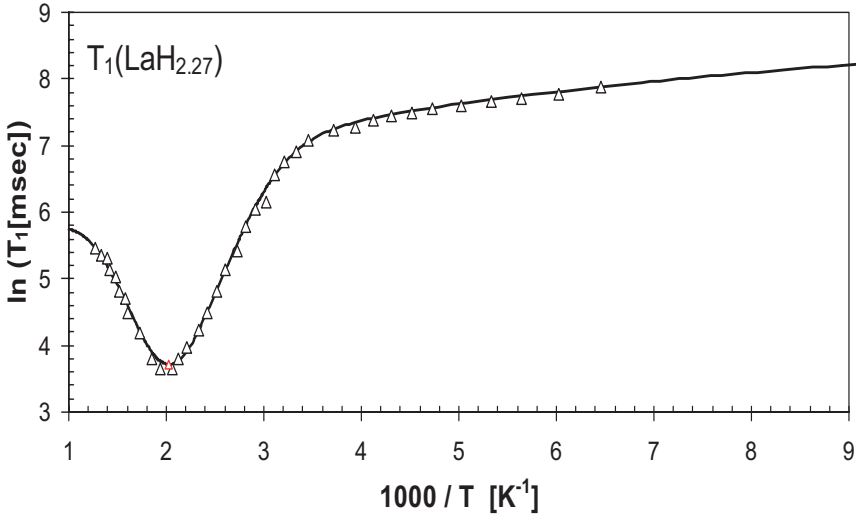


Figure 5. Experimental $T_1(T)$ points shown in Fig. 3 represented by the theoretical curve.

5. Conclusions

1. Figures 4 and 5 suggest that the ordering process taken into account by changes of the corresponding sum over octa-hydrogen positions in (5), does not influence significantly on the spin-lattice relaxation time. In this connection it has to be noted that in hydrides LaH_{2+c} besides the ordering subsystem of H_O -atoms there exist as well two unchanged subsystems - H_T -atoms and metal atoms, due to which changes of the mentioned sum in (5) are masked. In transition metal hydrides (Nb-H , V-H) the situation is better, as all hydrogen atoms are involved in the ordering process.

2. In spite of the results presented in Figs. 4 and 5, we suppose that the ordering processes can influence on the $T_1(T)$ dependences on modifying the hydrogen mobility by variations of the activation energy E_a . This effect was pointed out in [5] and in a different way discussed in [6]. We hope that subsequent investigations will illuminate this problem.

Acknowledgements

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CREATION OF HYDROGEN - SELECTIVE TUBULAR COMPOSITE MEMBRANES BASED ON Pd-ALLOYS: I. IMPROVEMENT OF CERAMIC SUPPORT WITH Ni LAYER DEPOSITION

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Abstract. Perspective alternative to expensive dense Pd-membranes are composite membranes with porous ceramic supports allowing considerable reduction of Pd (Pd alloy) layer thickness and membrane cost and ensuring at the same time enhanced permeability and good operating ability. However commercially available porous materials can not be directly used. The development of tubular composite α -Al₂O₃ -based supports for Pd-containing metal membrane is reported. Their distinction consists in using metal nickel, which is analog of palladium in many respects, for the modification of the porous structure of ceramic substrates. Magnetron sputtering is the most perspective for support modification with Ni layer and the following Pd-thin film deposition.

Keywords: Palladium, alumina, composite membranes, membrane preparation, nickel, hydrogen, sputtering

1. Introduction

Application of homogeneous dense metal membranes based on Pd-containing alloys allows effective production of high-purity hydrogen from various technological gases. One of the main application is production of CO-free hydrogen for fuel cells. Perspective alternative to these expensive dense membranes (with thickness not less than 50 μm) is development of composite membranes with porous supports allowing considerable reduction of Pd (Pd alloy) layer thickness and membrane cost and ensuring at the same time enhanced permeability and good operating ability. Porous ceramic, glass, stainless steel can be used as supports. The main problem here is to prepare supports with such porous structure which, first, would allow to produce defect-free thin selective Pd - containing layer; and, second, have good performance properties and transport parameters in hydrogen media at high temperature. And finally, cost of such supports should be significantly lower than that of traditionally used in Russia Pd – alloy foils with thickness of 50 μm . According to the estimates the mean pore diameter in the support surface layer should not be larger than 0.1 μm . Therefore commercially available porous materials cannot be directly used. Hence for the production of high-temperature composite membrane with Pd – based selective layer it is necessary to select supports satisfying necessary working conditions and to modify the surface for finishing deposition of thin selective Pd-alloy layer.

Several authors tried to prepare thin Pd-layers on porous supports. Methods usually used were CVD, electroless plating [1,2], sputtering [3-5]. For example Pd/Ni alloy membranes on porous stainless steel disks have been fabricated by vacuum electrodeposition technique [6]. Authors indicated that pore size, defects and surface roughness of substrate could affect deposition therefore special pretreatment was needed (authors used Ni powder and CuCN solution). Palladium (3 μm thickness) and palladium – silver alloy (1.6 and 1.8 μm thickness) membranes on modified tubular alumina membranes were prepared by electroless plating [1]. Ultrathin palladium – silver alloy membranes (250-500 nm) were deposited on ceramic support by RF magnetron sputtering [3]. The use of a pinhole-free γ -alumina support appeared to be the key for high-quality membrane creation. Therefore it was necessary to use sol-gel derived γ - Al_2O_3 support. Authors of [4] also indicated that substrate type (surface roughness) was one of the critical parameters for the synthesis of the composite Pd/ceramic membranes. Gas-tight Pd films (< 500 nm) with good adhesion could be coated on sol-gel fine pore γ -alumina support but not on α -alumina supports. Prior to Pd deposition on porous α - Al_2O_3 – disks it was also necessary to produce multi-layers of γ - Al_2O_3 on the support surface [7].

In this work for the first time magnetron sputtering (technologically effective method) was used for the modification of the tubular α -alumina ceramic support of the composite Pd – membrane. This modification could be realized due to the choice of Ni as hydrogen permeable metal instead of γ - Al_2O_3 layers. It allows to use total effective cross section of the surface porous structure of the support in high temperature process of hydrogen purification by Pd membrane.

2. Experimental and Discussion

Manufactured in Russia (TU - 3113-001-001739 01-95) mesoporous ceramic α - Al_2O_3 - tubes with the inner diameter of 6 mm and the outer diameter of 8 mm and length of 120-250 mm have been used as porous support. Microstructure, morphology, composition and other properties of the initial ceramic and deposited coatings have been investigated by atomic emission spectroscopy, X-ray diffraction (using Cu K_α radiation), scanning electron microscopy (S-570 Hitachi) and bubble point method. Gas permeation tests have been performed for nitrogen and helium by volumetric method using a soap bubble rotameter and also by gas chromatography.

Porous structure of the outer support surface has been modified by deposition of the additional layer of metal Ni. Two vacuum condensation techniques have been used for nickel deposition: dc ion magnetron sputtering and electron beam evaporation. To produce coatings on tubes additional installation for dc sputtering has been designed.

Microstructure of commercial alumina ceramic used as a support in this work is shown in Fig. 1. According to XRD, atomic emission spectroscopy and SEM data this membrane consists of a coarse α - Al_2O_3 – tube coated with finer layer of α - Al_2O_3 – tube (thickness of 40-60 μm). Traces of B, Ca and Si are detected by atomic emission spectroscopy. Pore sizes in the barrier layer of these tubes vary in the rather wide range from 0.05 to 0.5 micron, mean pore diameter being 0.2

micron. Such structure ensures high permeation flux. Selectivity for test gases (He/N_2) varied in the range 1.2-2.1 which is less than theoretical value for Knudsen regime (2.65). According to our estimates pore diameter not larger than $0.1 \mu\text{m}$ corresponds to this regime.

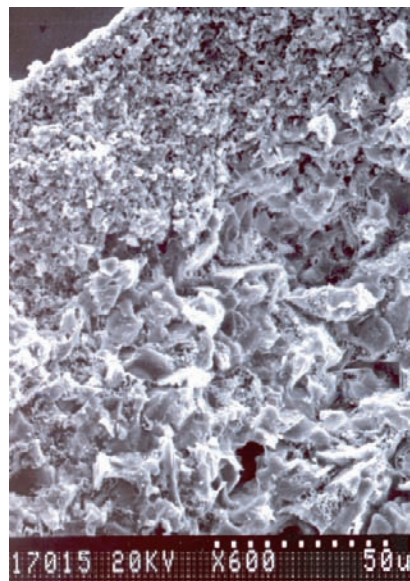


Figure 1. Microstructure of a commercial alumina ceramic used as a support.

Ceramic α - Al_2O_3 – tubes used in the present work have high thermal and chemical stability, mechanical strength and durability as has been shown by tests carried out in our previous works [8,9]. As was said above good results have been obtained in [7] for porous stainless steel supports. However ceramic supports are much more resistant to high temperatures and corrosion. Moreover they are produced commercially in tubular form which compared to the flat one provides effective membrane sealing, higher packing density in the apparatus and enhanced thermal stability of the barrier layer. Tubular shape is very perspective for application in membrane (or even catalytic membrane) reactors similar to those proposed for hydrogen purification and continuous hydrogen generation from methane and methanol [10-12]. Tubular composite membrane can be used in such reactors. Porous α -alumina tube manufactured by NOK Co. with void fraction of 0.43 and average pore size of $0.15 \mu\text{m}$ was used as Pd-membrane support in [13]. The tubes have an outer diameter of 2.0 mm and internal diameter of 1.6 mm. The length of membrane was 10 cm. However activation of alumina surface by seeding with palladium nuclei prior to electroless Pd plating was necessary in this case.

All previous results show that coarse α - Al_2O_3 support surface is not suitable for the direct deposition of high quality Pd (Pd alloy) films. Alumina ceramic supports with γ - Al_2O_3 layers successfully used for Pd-membrane preparation in

some other works cannot be used in gas separation industry because they are not stable enough. The main idea of our approach is to modify porous structure of the support by universal technologically effective method using metal which is less expensive than Pd but as well as Pd is hydrogen – permeable metal. This metal should be stable in high temperature technological processes, e.g. hydrocarbon steam reforming. It is desirable to use Ta, Nb, V which are more permeable than Pd according to several publications [14-16] however they are also expensive and long-term performance of such membranes is yet to be established [17].

In our present work we use Ni for the support modification (Ni-rich alloy can also be used). Nickel, as well as palladium, is excellent catalyst of molecular hydrogen dissociation (see Table 1 presenting some hydrogen diffusion parameters in nickel and palladium known from the literature [18]), and allows to use the total effective cross section of the surface porous structure of the support in high temperature processes. The possibility of Ni application for membrane preparation has been studied in several works. Fe can also be used as was shown by measurements of hydrogen permeability through Pd, Ni and Fe membranes [19] but Pd-membrane with such support would have limited application (only in the media without water vapor). Dense Pd-coated V-Ni alloy membranes have been prepared in [20]. Ni-P amorphous alloy/ceramic membrane with high selectivity and permeability for hydrogen compared to those of γ -Al₂O₃/ceramic composite membrane has been obtained by modified electroless plating [21]. Ultrathin Pd/Ni alloy membranes (typically 78% Pd and 22%Ni) with high hydrogen permeances and selectivities have been fabricated on porous stainless steel disks by vacuum electrodeposition technique [6].

TABLE 1. Some hydrogen diffusion parameters in nickel and palladium [18]

Metal	$t, ^\circ\text{C}$	$D_0, \text{cm}^2/\text{s}$	$Q_{\text{act}}, \text{kJ/mol}$
Ni	336-1400	6.9×10^{-3}	40.5
	125-1325	7.85×10^{-3}	40.8
	180-430	5.18×10^{-3}	40.0
Pd	0-650	6.0×10^{-3}	24.5
	-77-725	2.9×10^{-3}	22.2

D_0 - diffusion coefficient

Q_{act} - diffusion activation energy

We consider vacuum condensation technique as the most perspective for support modification and the following Pd (Pd alloy) thin film deposition. This technique enable to produce coatings as thin films of high purity and practically any composition on various supports including porous ones. Several recent publications underline that use of vacuum deposition techniques, especially magnetron sputtering, is very perspective for development of ceramic based membranes. For example, it was shown that dc magnetron sputtering can be used for Pd-Ag – membrane fabrication [7]. Authors prepared Pd-Ag films on V-15Ni membrane by co-sputtering of separate Pd and Ag targets. Magnetron sputtering has additional advantages – high efficiency of material use, high adhesion and uniform thickness of the coating. It should be noted that for other methods of Pd

(Pd alloy) deposition support pretreatment (cleaning) is necessary. For example the tubes used in [13] for Pd electroless plating were cleaned by sequential washing with water, ethanol and acetone under ultrasonic irradiation before alumina surface activation. As was said above at Pd vacuum electrodeposition special support pretreatment was also needed [6]. Even when magnetron sputtering was used for Pd deposition support surface had to be pretreated before deposition of $\gamma\text{-Al}_2\text{O}_3$ additional layers: $\alpha\text{-Al}_2\text{O}_3$ disks were polished with sand paper and clean in ultrasonic bath (acetone) [4]. In the present case special pretreatment of the support is not necessary as it occurs simultaneously with modification.

In our earlier works we have prepared various Ni-containing films by vacuum condensation technique and investigated their structure and properties depending on preparation conditions. Poly- or monophase Ni (and Ni-Al) layers with different microstructures and surface morphology were obtained by electron beam evaporation followed by heat treatment [22]. Continuous and highly adherent to the substrates Ni (and Ni-Al) layers were deposited by magnetron sputtering of Ni (or Ni-Al alloy) target. Film thickness was 5-10 μm . Coatings on powder, granules were obtained by magnetron sputtering of a composite Ni-Al target. Other Ni-rich films (La-Ni, Pr-Ni, Ni-Zr) were produced using magnetron sputtering [23,24]. Intermetallic targets LaNi_5 , PrNi_5 , ZrNi were used. Amorphous and polycrystalline La-Ni and Zr-Ni films with thickness 3-50 μm were obtained, film composition changing depending on substrate position relative to the magnetron axis. Depending on the substrate surface state and its temperature the deposited from PrNi_5 target films were crystalline with PrNi_5 structure or amorphous (water-cooled copper substrate) according to XRD data. Some of such films were deposited not only on plates but also on granules, ribbon etc. However for tubular supports used in the present work we had to modify magnetron sputtering technique. Special insert installation has been designed. Metal coatings with different thickness (5-8 μm) have been obtained on ceramic tubes. Ni coatings have been also prepared by electron beam evaporation for comparison. Sputtered coatings consisted of rather dense columnar grains and are highly adhesive to the surface of the tubular support. Their microstructure differed sharply from that of films obtained previously on dense flat substrates. It is known that if coatings are deposited at substrate temperatures that are low relative to the coating material melting point their structure typically consists of a columnar structure with voided boundaries which is superimposed on polycrystalline or amorphous structure [25]. Moreover, not only deposition conditions (support temperature, working gas type and pressure, geometry of sputtering, device characteristics etc.) determine the structure of coatings but also the support surface irregularities as high places on the support receive more coating flux. Therefore it is clear that thin dense Pd (Pd alloy) film cannot be deposited directly on coarse alumina surface. Choosing optimal parameters of deposition and layer thickness allows to obtain acceptable Ni grains size and consequently porous structure necessary for the successful Pd (Pd alloy) deposition. Necessary thickness of the Ni layer was defined by gas selectivity for test gases. Modification was considered to be finished when selectivity approached ideal values (according to Knudsen regime). According to our results deposition conditions in contrast to the layer thickness did not influence on this parameter

significantly. However they are very important for Pd (Pd alloy) thin film production.

The samples have been investigated by X-ray diffraction and SEM microscopy. Ni peaks at $2\theta = 44.5^\circ$ and $2\theta = 51.9^\circ$ can be seen on X-ray patterns of the samples obtained by the both vacuum deposition techniques (Fig. 2). They correspond to ASTM data 4-850 for Ni (peak $2\theta = 44.5^\circ$ (111), $I/I_0 = 100$ and $2\theta = 51.9^\circ$ (200), $I/I_0 = 42$).

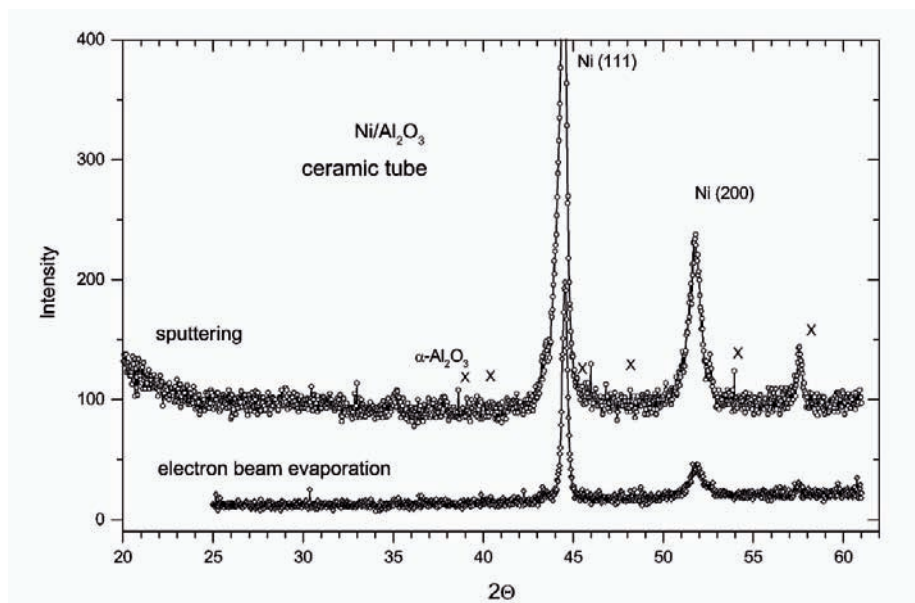


Figure 2. XRD pattern of the Ni-coated ceramic.

Weak peaks of the ceramic support are also seen. Ni peaks for the case of electron beam evaporation are sharper, crystallinity of the coating is higher compared to the magnetron sputtering case. This is also confirmed by SEM of nickel coatings obtained by magnetron sputtering (Fig. 3) and by electron beam evaporation (Fig. 4).

Alumina support modified with Ni is ready for palladium deposition which can be carried out in the same device. Pd (Pd alloy) deposition should be followed by additional thermal treatment for the complete inter phase diffusion of Ni and Pd.

3. Conclusions

Tubular composite α - Al_2O_3 -based supports for Pd-containing metal membrane have been developed. Their distinction consists in using metal nickel for the modification of the porous structure of ceramic supports. Nickel is analog of palladium in many respects it is also effective catalyst for molecular hydrogen

dissociation. All stages of the technological process of Pd-membrane production can be carried out in the same device by magnetron sputtering.

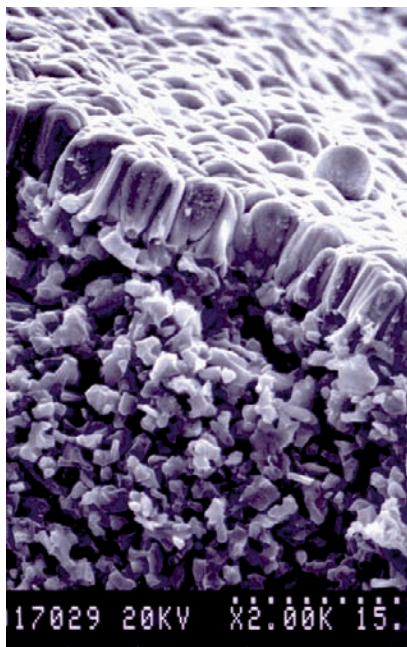


Figure 3. SEM of Ni/ α -Al₂O₃ membrane. Nickel coating obtained by magnetron sputtering.

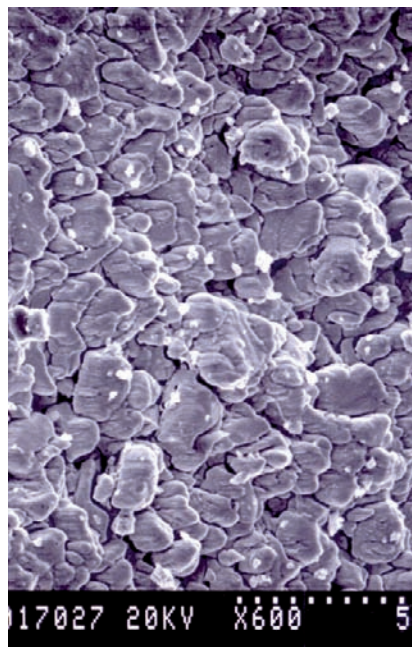


Figure 4. SEM of Ni/ α -Al₂O₃ membrane. Nickel coating obtained by electron beam evaporation.

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HYDRIDES FORMATION IN HOLLOW CYLINDER

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Abstract. The process of hydrogen absorption in a hollow cylinder with residual stresses has been considered. The latter ones occur in the material of products when carrying out different technological operations. The level and character of the residual stresses distribution change kinetics of diffusion migration of hydrogen atoms. The process of hydrogen absorption is described by a non-stationary diffusion equation in the field of forces under corresponding initial and boundary conditions. The analytical relations for the field of hydrogen atoms concentration have been given. If local concentration of the hydrogen atoms exceeds the solubility limit at given temperature, hydrides are formed in some metals (for example, in zirconium). Volume changes of the latter ones lead to forming microcracks on interphase boundaries. The hydride formation process depends on the level and nature of stresses distribution. The analytical analysis results are attracted for explaining physical mechanism of the hydrides formation in hollow cylinder with residual stresses.

Keywords: hydrogen atoms, residual stresses, hydrogen absorption kinetics.

1. Introduction

The residual stresses occur in the material of the products when carrying out different technological operations. The level and character of the residual stresses distribution have an essential effect on the diffusion processes kinetics. Thus, for example, substitution impurities of a large atomic radius migrate into the area of tensile stresses, and corresponding impurities of a small atomic radius migrate into the field of compression stresses. In this way decomposition of the solid solution in the field of residual stresses occurs [1]. The purpose of this paper is analyzing the hydrogen absorption kinetics in the hollow cylinder with the residual stresses. Choosing such a model system is caused by the following reasons. Firstly, it is possible to obtain residual stresses of different signs within the hollow cylinder by cutting and adding (excluding) part of the material with the following connecting the edges of the cut. Secondly, logarithmic dependence on a radial coordinate of the first invariant of the residual stresses tensor provides obtaining the exact

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analytical solution of the diffusion equation in the field of forces. And at last, proposed model analysis has a direct analytical application. Hydrogen absorption is considered to be one of the main tasks of hydrogen engineering.

For obtaining the residual stresses in the hollow cylinder, do as advised below. The edges of the cylinder cut are moved apart through angle ω and some deficit material is put there. The surrounding of the inner cylinder surface is in the tensile state, and the area of the outer surface is in the compression state. The hydrogen atoms interact with the residual stresses of the opposite signs. The interaction potential for dimensional effect is defined by the known relation [2]

$$V = -\frac{\sigma_{II}}{3} \delta v \quad (1)$$

where σ_{II} - first invariant of the residual stresses tensor, δv - change of volume of the metal when placing the hydrogen atoms. It is interesting to be noted that magnitude of δv is approximately equal for all metals and it is of $3 \cdot 10^{-30} \text{ m}^3$ [3]. For a hydrogen atom $\delta v > 0$ and therefore at $\sigma_{II} > 0$ (tensile stress), potential V takes a negative value. It corresponds to attraction of the hydrogen atoms to the area with the tensile stresses. In other words, the hydrogen absorption process depends on the character of the residual stresses distribution. The first invariant of the residual stresses tensor takes a form (flat deformation) [4]

$$\sigma_{II} = \frac{\mu\omega(1+\nu)}{2\pi(1-\nu)} \left\{ 1 + 2 \ln \frac{r}{R} + \frac{2\left(\frac{r_0}{R}\right)^2}{1 - \left(\frac{r_0}{R}\right)^2} \ln \frac{r_0}{R} \right\}, \quad (2)$$

where μ - shear modulus, ν - Poisson's ratio, ω - turning angle of the cylinder cut edges, r_0 and R - inner and outer hollow cylinder radius. Under other equal conditions the sign of σ_{II} depends on the angle of turning the cylinder cut edges. We take by convention $\omega < 0$, if $\sigma_{II} > 0$ onto the inner cylinder surface.

2. Hydrogen absorption kinetics

The hydrogen atoms absorption within the accepted model system is described by a non-stationary diffusion equation in the field of potential V under corresponding initial and boundary conditions [5]

$$\frac{1}{D} \frac{\partial C}{\partial t} = \Delta C + \frac{\nabla(C \nabla V)}{kT}, \quad r_0 < r < R, \quad (3)$$

$$C(r, 0) = 0, \quad C(r_0, t) = C_p^1, \quad C(R, t) = C_p^2,$$

where D - coefficient of the hydrogen atoms diffusion, C_p^1 and C_p^2 - equilibrium concentrations of hydrogen atoms on the inner and outer cylinder surfaces, k - Boltzmann's constant, T - absolute temperature. Physical sense of the initial and boundary task conditions (3) is quite obvious. At the initial time moment the hydrogen atoms concentration within the cylinder is equal to 0. The boundary conditions at $r = r_0$ and $r = R$ mean that the equilibrium concentration is kept on the boundaries of the area in accordance with the interaction potential. The process of the hydrogen absorption runs from the side of the inner and outer surfaces of the

hollow cylinder. Without loss a generality, let's consider the following character of the residual stresses distribution: extension on the inner surface and compression on the outer one. Such distribution of the residual stresses "extracts" the hydrogen atoms from the side of the outer surface and "retards" the hydrogen absorption from the inner surface.

Diffusion migration of the hydrogen atoms depends on the gradient of potential V . Thus, the constant relations (2) do not influence the diffusion process. In this case $\Delta V=0$ as V is a harmonic function. Taking into account (1) and (2), task (3) is mathematically formulated as follows:

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1-\alpha}{r} \frac{\partial C}{\partial r}, \quad r_0 < r < R, \quad (4)$$

$$C(r,0)=0, \quad C(r_0,t)=C_p^1, \quad C(R,t)=C_p^2.$$

Non-dimensional parameter α specifies the relation between the connection energy of a hydrogen atom with the residual stresses to the energy of heat motion

$$|\alpha| = \frac{\mu|\omega|(1+\nu)\delta v}{3\pi(1-\nu)kT}$$

In case of $|\alpha| \ll 1$, the residual stresses field is considered to be a small disturbance of a diffusion flow of the hydrogen atoms at the expense of the concentration gradient. For $|\alpha| \gg 1$ the residual stresses field gives main contribution into the diffusion process. When $|\alpha| \approx 1$, the diffusion flows of the hydrogen atoms are compared at the expense of concentration gradients and potential V . Let's evaluate magnitude $|\alpha|$ for the system Zr-H. Taking $kT = 10^{-20}$ J; $\mu = 4 \cdot 10^{10}$ Pa; $\nu = 0.3$; $|\omega| = 0.3$ rad; $\delta v = 3 \cdot 10^{-30}$ m³ we obtain $|\alpha| \approx 1$. Thus, take the non-dimensional parameter α being equal 1 in absolute value. This parameter sign depends on the character of the residual stresses distribution in the hollow cylinder. In case of $\omega < 0$ (tensile stresses on the inner surface), $|\alpha| = -1$. When changing the sign of the residual stresses, parameter α takes a positive value, i.e. $\alpha = 1$. The hydrogen absorption from the inner and outer surfaces of the cylinder obeys different laws. For qualitative analyzing the process kinetics, principle of superposition of the two tasks solution should be used. The first task describes the hydrogen absorption from the outer side of the surface, and the second one does it from the inner side. The principle of superposition follows from the diffusion equations linearity.

For $\alpha = -1$, the atoms concentration field is found from the task solution

$$\frac{1}{D} \frac{\partial C_1}{\partial t} = \frac{\partial^2 C_1}{\partial r^2} + \frac{2}{r} \frac{\partial C_1}{\partial r}, \quad r_0 < r < R, \quad (5)$$

$$C_1(r,0)=0, \quad C_1(r_0,t)=C_p^1, \quad C_1(R,t)=0.$$

The residual stresses change symmetry of the diffusion equation: the diffusion process within the hollow cylinder obeys the law of spherical symmetry. Conversion of the coordinate dependence decreases a rate of forming a concentrating profile from the hydrogen atoms. The physical essence of retarding the hydrogen absorption kinetics is caused by reducing the tensile stresses in the radial direction up to their change with the compression stresses. The hydrogen

absorption from the outer cylinder surface is described by the equation (non-dimensional parameter changes the sign)

$$\frac{1}{D} \frac{\partial C_2}{\partial t} = \frac{\partial^2 C_2}{\partial r^2}, \quad r_0 < r < R, \quad (6)$$

$$C_2(r,0)=0, \quad C_2(r_0,t)=0, \quad C_2(R,t)=C_p^2.$$

And again the residual stresses change the symmetry of the task: the diffusion process in the hollow cylinder obeys the law of flat symmetry. The hydrogen absorption rate increases from the side of the outer boundary. Acceleration of the process kinetics is caused by reducing the compression stresses in the radial direction, which are changed with the tensile stresses. The solution of tasks (5) and (6) is well known. Thus, it is not difficult to obtain the solution of task (4). This solution describes the hydrogen absorption kinetics from the two surfaces of the hollow cylinder at given character of the residual stresses distribution

$$C = C_1 + C_2 = \frac{C_p^1 r_0 (R-r) + C_p^2 r (r-r_0)}{r(R-r_0)} +$$

$$+ \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n r C_p^2 - r_0 C_p^1}{r} \cdot \frac{\sin \frac{\pi n (r-r_0)}{R-r_0}}{n} \exp \left(- \frac{\pi^2 n^2 D t}{(R-r_0)^2} \right). \quad (7)$$

The hydrogen absorption kinetics obeys the exponential law and depends on the equilibrium concentrations on the area boundaries. The latter ones is defined by the level of the residual stresses on the corresponding boundaries

$$C_p^1 = C_0 \exp \left(\frac{\sigma_{tt} \delta v}{3kT} \right)_{r=r_0}, \quad C_p^2 = C_0 \exp \left(\frac{\sigma_{tt} \delta v}{3kT} \right)_{r=R}, \quad (8)$$

where C_0 - concentration of hydrogen atoms on the cylinder surfaces after dissociation of molecules. On the inner surface (tensile stresses) $C_p^1 > C_0$, and on the outer one (compression stresses) $C_p^2 < C_0$.

3. New phases formation in the stresses field

The new phases are characterized by considerable volume changes in relation to the basic material. The stresses occur on the interphase boundaries, and microcracks are formed. The example of such damage is metal embrittlement when forming hydride phases. The internal stresses also have an effect on kinetics of a new phase growth. Let us consider the residual stresses in a hollow cylinder. Maximal concentration of the impurity atoms occurs on the area boundary, where the new phase formation takes place. Its further growth is realized at the expense of impurity atoms diffusion. The task of defining kinetics of the new phase growth in the hollow cylinder is mathematically formulated as follows

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial r^2} + \frac{1+\alpha}{r} \frac{\partial C}{\partial r},$$

$$C(R_1, t) = C_2, \quad C(r, 0) = C_0 \quad (r \geq R_0), \quad C(\infty, t) = C_0, \quad (9)$$

$$(C_1 - C_2) \frac{dR_1}{dt} = D \left\{ \left| \frac{dC}{dr} \right| + \left| \frac{C\alpha}{r} \right| \right\}_{r=R_1},$$

where R_0 - radius of the a phase centre, R_1 - current radius of a new phase. The rest notations are correspond to the ones accepted before. On the moving interphase boundary the concentration of the impurity atoms is changed in leaps and bounds: $C=C_1$ for the new phase and $C=C_2$ in the surrounding matrix ($C_1 > C_2$, $C_2 < C_0$, where C_0 - average concentration of the impurity atoms). It is supposed that a typical size of the new phase centre is considerably less than the hollow cylinder thickness. Such supposition allows us to consider the new phase growth in an unlimited matrix and obtain the analytical solution of task (9). Change of the new phase radius obeys the law $R_1(t) = \delta \sqrt{Dt}$, where δ - dimensionless parameter of the task. Its value is determined from the mass balance equation on the interphase boundary. For $\alpha = -1$ approximately to "stationary interphase boundary" we will obtain a quadratic equation for determining parameter δ

$$\delta^2 - \frac{2\delta}{\sqrt{\pi}} \left| \frac{C_2 - C_0}{C_1 - C_2} \right| - \left| \frac{2C_2}{C_1 - C_2} \right| = 0. \quad (10)$$

If $\alpha = 0$, the internal stresses field is not taken into account. For determining parameter δ_1 of relations $R_1(t) = \delta_1 \sqrt{Dt}$ we will obtain a transcendental equation

$$\delta_1 = \frac{2}{\sqrt{\pi}} \left| \frac{C_2 - C_0}{C_1 - C_2} \right| \frac{K_1 \left(\delta_1 \frac{\sqrt{\pi}}{2} \right)}{K_0 \left(\delta_1 \frac{\sqrt{\pi}}{2} \right)} \quad (11)$$

where $K_0(x)$ and $K_1(x)$ - modified cylindrical functions. Keeping commonality, we take $C_0 = 2 \cdot 10^{-4}(\text{at})$, $C_2 = 10^{-4}(\text{at})$ и $C_1 = 3 \cdot 10^{-4}(\text{at})$. From the solution of equations (9) and (10) we obtain $\delta = 1.3$ and $\delta_1 = 0.8$. The internal stresses field accelerates the diffusion process of the new phase growth. The other values of the boundary conditions change a numerical value of parameters δ and δ_1 . The volume changes of the new phase cause the stresses on the interphase boundary. If the stresses level exceeds a critical value, the microcracks formation takes place. The material damage is observed in a macroscopic scale. Simulation of this process also includes kinetics of the new phase growth.

4. Conclusions

The internal stresses have an essential effect on kinetics of diffusion processes in metals and alloys. When changing the concentration of the alloying elements, reducing the strength material characteristics takes place, and probability of damaging under the external load increases. Simulation of the material damage process taking into account the internal stresses field includes a definite sequence of the mathematical operations. These operations define the algorithm of the material damages calculation: definition of the first invariant of the internal stresses tensor, mathematical formulation of the task of impurity atoms diffusion followed by the new phase formation. Kinetics of the impurity atoms segregation obeys the equation of a parabolic type under corresponding initial and boundary conditions. The complicated coordinate dependence of the internal stresses field makes

difficulties in obtaining the analytical solution of the diffusion equation in the stresses field. A good exclusion from the general rule is the internal stresses with a logarithmic coordinate dependence. Such dependence allows the analytical solution of the diffusion kinetics task to be obtained. It is caused by the fact that potential V is a harmonic function, and its gradient ∇V is inversely proportional to the radius in the polar coordinate system. The analytical dependences for the impurity atoms concentration taking into account the residual stresses in the hollow cylinder have been obtained. Under the definite conditions some changes in the diffusion equation symmetry have been revealed. Kinetics of the impurity atoms segregation for cylindrical geometry runs according to the flat symmetry law. It increases a rate of the impurity segregation. The results of mathematical simulation of the material damages are of interest for ensuring operational safety of structural elements of modern equipment.

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INTERBAND ELECTRON TRANSITIONS IN THE ALLOYED C₆₀ FILMS WITH THE IONIC DEFECT FORMATION

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Abstract. The spectral dependence of photoluminescence and optical conductivity for the solid C₆₀ and Cd-C₆₀ films (with the admixture of C₇₀ fullerenes) are studied under irradiation by argon ions with different doses. The fragmentation of the C₆₀ molecules and the formation of the radiation defects, which are accompanied by appearance and increase in the intensity of the new component of the excitons emission, by decrease in the high-frequency optical conductivity $\sigma(E)$ and approach of its spectral dependence to an analogous characteristic for the amorphous carbon films are observed with an increase in the radiation dose. This testifies that with the destruction of the molecules structure by ions the growth of the number of electrons, which are in the sp^2 -hybridized state takes place. Furthermore, with the appearance of radiation defects the formation of the traps of the free charge carriers, which lead to a total decrease in the optical conductivity occurs.

Keywords: radiation defects; optical transitions; electron structure; fragmentation of fullerenes

1. Introduction

The formation of radiation defects under irradiation of the fullerene films by the bombarding particles leads to the essential modification of electronic subsystem, which determines their optical and electrophysical properties. However, the mechanisms of radiation defect formation with the use of different types of irradiation and dose load, and also the nature of a change in the electronic properties in this case are studied insufficiently. It is necessary to note that in the case of the condensed state of fullerenes not only the radiation damages of the molecular polyhedrons, which by themselves influence the redistribution of

electron density and transition energy in the region of the energy gap and other molecular transitions take place [1-2]. The impurities of carbon, inculcated in the intercalated positions of the crystal lattice, as a result of their radiation displacement from the frame of molecules during the high-energy electronic irradiation are played notable role too [3]. The charge exchanges between interstitial atoms and molecules is accompanied in this case by essential reconstruction of the density of the electronic states of vacant energy bands. It is assumed [4] that under the external influence the fast electrons is possible the multiple impact ionization of the fullerene molecules in a crystal lattice, which is responsible for the formation of the conduction electrons and radiation current. Its value is determined not only by the concentration of the obtained conduction electrons, but also by the generatable radiation defects, which are been the traps of free charge carriers. In the case of the excitation of the condensed state of fullerenes by relativistic electrons and synchrotron radiation [5] the damages of polyatomic polyhedrons are not limited to the creation only of point defects, but also by the presence of the fragmentation of molecules. The modification of the atomic structure of fullerenes due to the destruction of the molecules structure is more noticeable under their interaction with the heavy ions. Even the insignificant radiation destruction of molecular structure [6] has a noticeable effect on reconstruction of the electron structure of HOMO-LUMO region, and also in energy range of valence and vacant states, that join to the energy gap.

The variety of the manifestation of interaction of external emission with the fullerene molecules, connected by the Van der Waals forces in the crystals, makes difficult understanding the mechanisms of the modification of their physical properties. Therefore, the study of these properties, in the first place, of changes in the electron structure under the action of different bombarding particles is of interest.

In this work the studies of optical characteristics, including photoluminescence and optical conductivity $\sigma(E)$ of the C_{60} and $Cd-C_{60}$ films with different radiation doses by argon ions with the energy of 0,3 keV are carry ouied. The films of fullerenes C_{60} and $Cd-C_{60}$ with the admixture of the C_{70} molecules (~ 10 mass %) are precipitated out to the substrates from the stainless steel (temperature of the substrate was equal to 473 K) during the vacuum sublimation [7]. Photoluminescence was studied with the laser excitation with a wavelength of 514,5 nm [8]. Optical conductivity was measured with the use of a method of spectral ellipsometry [9-10].

2. Experimental results and discussion

The study of the radiative recombination of excitons makes it possible to investigate the influence of the radiation-stimulated destruction of C_{60} fullerenes (partially of C_{70}) on changes of the singlet states within the energy gap. It is known that the emission of excitons in this case is the result of the presence of own dimeric traps [11] and X-centers, caused by the chemically bound with fullerenes and intercalated impurities [8], and also of taking into account the corresponding phonon states.

Figure 1 gives the spectral dependence of the emission of electrons for the C_{60} films, processed in the plasma of the glow discharge of argon. It is evident that the presence in a crystal lattice of the C_{60} molecules is not manifested in the spectra of photoluminescence (the basic mechanism of the radiative recombination of singlet excitons for C_{60} fullerenes corresponds to the energy of $\sim 1,8$ eV). With an increase in the dose of ionic irradiation the growth of the value of relative intensity in the region of the basic peak of photoluminescence ($\sim 1,7$ eV) is observed, while the behavior of peak near the energy of 1,5 eV remains constant. Furthermore, it is seen that an increase in the intensity of the component of basic peak near the energy position of 1,73 eV and the shift of this emission band to the side of higher energies occurs. A similar tendency in a change in the spectrum of photoluminescence is manifested also for the Cd- C_{60} films (Fig. 2). In the nonirradiated sample the bands of the emission of excitons near the energies of 1,5 and 1,65 eV are noticeable, that is the consequence of localization of excitons on the X-traps [3], to formation of which contributes a cadmium. The relative intensity of the main peak of singlet emission also grows, and its high-energy component displaces to the great significances of energy. This peak becomes doublet with the preservation of the wide emission band, which overlaps the low-energy bands near the energies of 1,5 and 1,65 eV.

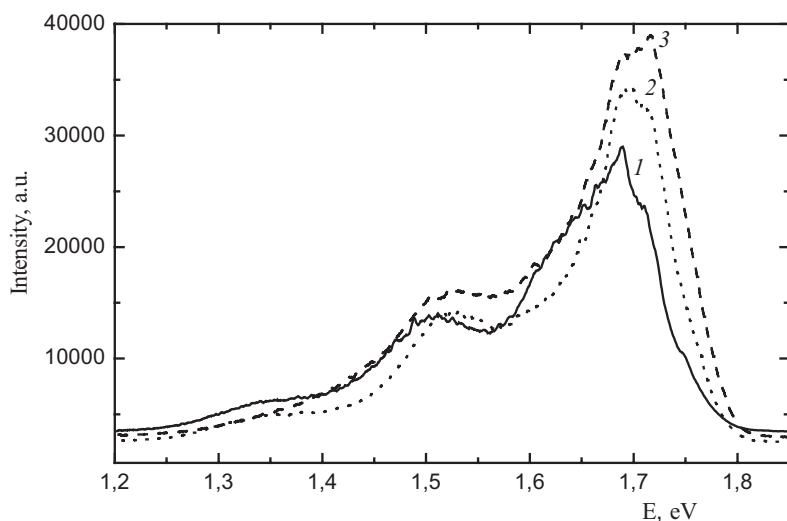


Figure 1. Spectra of photoluminescence for the C_{60} films (with the admixture of C_{70} fullerenes) under irradiation by the argon (Ar^+) ions: 1 – the initial, nonirradiated state; 2 – the radiation dose is 8×10^{14} ion/cm²; 3 – 27×10^{14} ion/cm². The substrate is the stainless steel, $d = 1200$ nm, $T_{melt} = 473$ K, $\lambda = 514,5$ nm, $T = 77$ K.

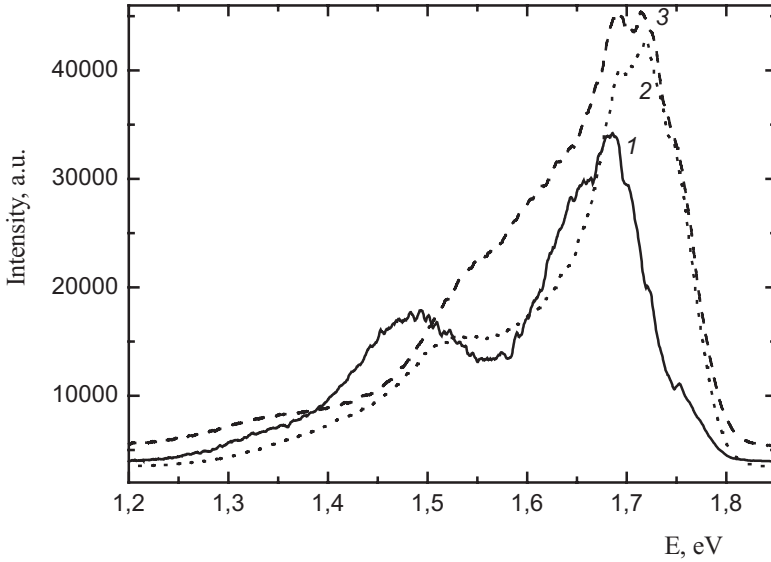


Figure 2. Spectra of the excitons emission for the Cd-C₆₀ films (with the admixture of C₇₀ fullerenes) under irradiation by the argon (Ar⁺) ions: 1 – the initial, nonirradiated state; 2 – the radiation dose is 8×10^{14} ion/cm²; 3 – 27×10^{14} ion/cm². The substrate is the stainless steel, $d = 1200$ nm, $T_{\text{melt}} = 473$ K.

Thus, the ion irradiation leads to the modification of the structure of electronic states in the energy gap of HOMO-LUMO. In this case the electron spectra of all traps both dimeric, and impurity, are affected, that indicates about the changes in the atomic structure of fullerenes as a result of their radiation destruction and about the accumulation of radiation defects in a crystal lattice. The effects of radiation exposure indicated affect also distribution of electron energy in the valence and vacant bands, that specifies the transformation of optical interband transitions.

As one can see from Fig. 3 (the spectral dependence of optical conductivity $\sigma(E)$ in the interval of interband transitions) the greatest changes are observed for the high-frequency conductivity, caused by $V_1 \rightarrow C_3(h_u \rightarrow h_g)$ transition [9-10]. This transition proves to be most sensitive to changes in the electronic states and generation of strapping sites of free charge carriers with the radiation damages and the formation of radiation defects. Actually, the ion irradiation even with the insignificant dose leads to a significant increase in the value of the optical conductivity in the region of energy ~ 4.25 eV. The energy levels, which correspond for this transition, are splited, since in a $\sigma(E)$ curve (curve 2) near the energy of 4.25 eV it is possible to isolate several maximums of optical conductivity.

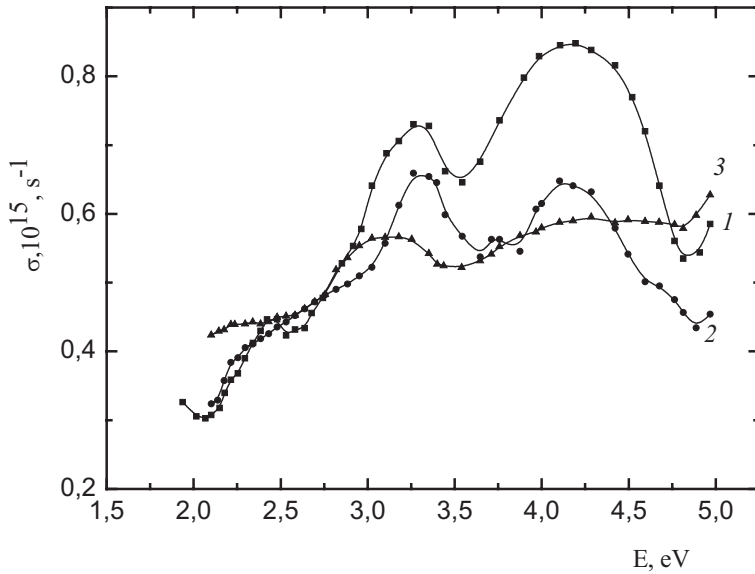


Figure 3. Spectral dependence of the optical conductivity $\sigma(E)$ of the C_{60} films (with the admixture of C_{70} fullerenes) under irradiation by the argon (Ar^+) ions: 1 – the initial, nonirradiated state; 2 – the radiation dose is 8×10^{14} ion/cm²; 3 – 27×10^{14} ion/cm². The substrate is the stainless steel, $d = 1200$ nm, $T_{\text{melt}} = 473$ K.

Value $\sigma(E)$ in entire energy range decreases. Several reasons for the observed increase of $\sigma(E)$ are possible. One of them there is the fragmentation of molecules, connected with the destruction of their structure, which leads to the redistribution of electron density [5-6]. The change in the spectra of valence electrons indicating their similarity with the spectra of the amorphous carbon films [5], whose structure consists of diamond-like sp^3 -hybridization of carbon atoms phases. The latter can be considered as the totality of the fragments of graphite planes and distorted parts of the fullerene molecule [12]. As a result of the ion bombardment of the diamond-like films of carbon [13-14] the changes in the electron spectra as the consequence not only of the amorphization of films, but also of the disintegration of metastable diamond-like nanoparticles occur. With the modification of thin films by the metals [15-16] the similar changes appear as a result of interaction of metals with the graphite hexagonal rings in the graphite-like nanoclusters. Moreover, it is known [10, 17-18] that depending on the atomic arrangement of metals relative to the C_{60} molecule and each other the electron states of such clusters can differ essentially.

It is possible to assume that in the case of the C_{60} films irradiated by Ar^+ ions the fragmentation of molecules, which leads to the growth of the concentration of carbon atoms, whose electronic state strives to the sp^2 -hybridization, i.e., to the more graphite-like phase occurs. With the formation of radiation defects, in

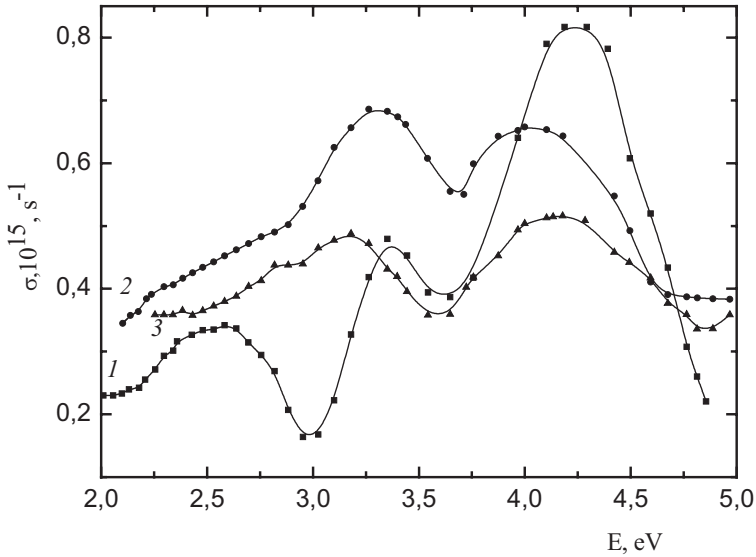


Figure 4. Spectral dependence of the optical conductivity $\sigma(E)$ of the Cd-C₆₀ films (with the admixture of C₇₀ fullerenes) under irradiation by the argon (Ar⁺) ions: 1 – the initial, nonirradiated state; 2 – the radiation dose is 8×10^{14} ion/cm²; 3 – 27×10^{14} ion/cm². The substrate is the stainless steel, $d = 1200$ nm, $T_{\text{melt}} = 473$ K.

particular, the displaced atoms of carbon in the positions of intercalation, is possible the formation of the inculcated local electron states, that is observed on the appearance of additional bands of the emission of excitons. From one side, these levels can contribute to the generation of additional optical passages, while with another side they are played the role of the traps of free charge carriers, that leads to a decrease in the values of optical conductivity. With an increase in the radiation dose (curve 3) the nature of optical conductivity changes essentially. It is evident that the band of optical absorption near the energy of 4,25 eV disappears, and motion of $\sigma(E)$ is nearer to the behavior of optical conductivity for the amorphous carbon. It is obvious that an increase in the dose of ion irradiation leads to the filling of traps and therefore the $\sigma(E)$ drop slows down. During the ion irradiation it is difficult to estimate the contribution of the displaced atoms of carbon. It is known that with the insignificant doses of electron irradiation [3] the increase in the optical conductivity, which is caused by the transfer of charges from the interstitial atoms of carbon to C₆₀ fullerenes is observed. As a result of ion irradiation the inverse effect occurs, that is undoubtedly connected with the partial destruction of molecules. In the films, obtained during the simultaneous precipitation of the C₆₀ molecules (with the admixture of C₇₀ fullerenes) and atoms of cadmium, the process of the fragmentation of fullerenes is the less active than in the case of the absence of impurities. However, all basic features of $\sigma(E)$ dependence on the radiation dose remain (Fig. 4).

It is possible that partially decrease of $\sigma(E)$ is determined by the possible dispersion of fullerenes, although it is not essential with the selected energy of $E_{Ar^+} = 0,3$ keV. Possibly, the $\sigma(E)$ drop is connected with the formation of Cd-C complexes, which create the deep traps for capture of free electrons. The appearance of such traps in energy range of HOMO-LUMO confirms in the formation of the new bands of the emission of excitons for the Cd-C₆₀ mixture (Fig. 2).

3. Conclusions

The irradiation by ions, which leads to the fragmentation of the solid C₆₀ films, is accompanied by the appearance of the new component of the emission of excitons. The intensity of this component of photoluminescence grows with an increase in the radiation dose. In the Cd-C₆₀ mixture also noticeably grows the emission of the excited molecules in the X-centers, to appearance of which it can contribute Cd or Cd-C complexes due to the transition to the inculcated positions of the displaced carbon atoms from fullerenes with the radiation damages of molecules. The appearance of the different kind of the deep traps of free charge carriers with the generation of radiation defects together with the structural destruction of molecules with their fragmentation by the bombarding ions leads to the complex processes of changes in the optical conductivity with an increase in the radiation dose. These changes are the result of the imposition of the electronic concentration redistribution between sp^3 - and sp^2 -hybridized states of the carbon atoms and electron mobility with the presence of their traps as a result of the creation of radiation defects. The manifestation of the defects indicated is characterized by disappearance of the bands of the optical conductivity with an increase in the radiation dose, which are formed because of the presence of the specific molecular orbitals, and also by total $\sigma(E)$ drop. With the fragmentation of molecular polyhedrons the optical conductivity approaches to be similar to $\sigma(E)$ for the films of amorphous carbon, that is accompanied by an increase in the concentration of sp^2 -hybridized states of carbon atoms.

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COMPUTER SIMULATION OF THE ELECTRON BEAM IRRADIATION EFFECT ON THE MODIFICATION OF CARBON NANOTUBES

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Abstract. The scientific goal of the present work is to study how carbon nanotube's (CNT) physical properties (electron structure including band gap, atomic structure, transport and emission characteristics) are transformed under the electron beam irradiation and depend on the concentration and type of defects induced by the beam. In particular, we have established how these properties can be modified in a controlled way so as to allow the radiation induced creation of heterostructures and fabrication tunneling barriers for the single electron transistor in the single- or multi-walled CNT. Theoretical description of the above mentioned subjects, processes and corresponding calculations are based on the PM3 approximation, density functional theory and tight-binding models.

Keywords: carbon nanotubes; electron beam irradiation; computer simulation

1. Introduction

CNT are one of the most perspective building blocks for producing nanoelectronics devices because they can have dielectric, semiconductor or metal properties depending on their chirality. Now, two ways are intensively being investigated to apply them: *a)* as wires for linking devices of molecular scale, for example on basis of fullerenes [1]; *b)* as constituents of such devices [2]. Producing of a junction between nanotubes is a key problem on the second way. Recently several methods are proposed for its solution. The first is a producing of heterojunctions Y-shape, T-shape and more complex ones during nanotube growth [3-5]. Here the most difficult problem is choice of optimal conditions: a growth technique, temperature, an atmosphere, a catalytic agent, a substrate, etc. However, if a successful choice of these parameters was found, then mass manufacturing can apparently be achieved with high-ideality junctions [6]. We shall note, this method apparently also allows

producing the 3-D junctions with more than four tube-branches emerged from one node. Another method is so called welding or tailoring nanotubes by using beams of particles, namely electrons and/or ions [2,7-10]. Experiments [2,7-10] have shown an opportunity of such tailoring of nanodevices. In opposite the first method, this process obeys an immediate control and gives more possibilities for producing junctions with prescribed properties and also allows using various auxiliary components and conditions during irradiation. So, experiment [11] has shown that fluorination of the multi-walled CNT (MWCNT) drastically influences on their ability to transformations under particle beam, and in [12] it has been shown that presence nanodrops of water inside the MWCNT leads to punching of holes in their walls under focused intensive electron irradiation. It is necessary to underline that characteristics of particles beam welded of the nanotubes should obey some requirements which are essentially different from those needed for ion implantation in microelectronics [13], or for fullerite polymerization by electron beam [14]. Main reason of it is small size of target reached about several nanometers, and absence of plenty surrounding atoms which influence on particle-atom collisions.

Electronic properties of the nanojunctions nowadays are intensively investigated theoretically [15, 16]. In these articles it has been found that atomic structure of junction essentially influences on conductance type, conductance is suppressed when disorder in the junction area increases, and even quantum dots can be formed therein [15].

2. Model

It is supposed that nanotube welding can be treated as a physicochemical reaction transferring the system from one equilibrium state in another. We call as the ideal junction such one, where all atoms are located most closely to two cylindrical surfaces with traversed axes and diameters $D_{1,2}$ linked with nanotube type by relations $D = \sqrt{m^2 + n^2 + mn} \sqrt{3} d_0 / \pi$, where $d_0 = 0.142$ nm is interatomic distance in graphite layers. Optimal configurations of various ideal junctions can be found by minimizing energy of system using molecular dynamics simulation or by more accurate methods [15,16]. An area is called junction area if it lies around a point where axes intersect or approach on a minimal distance, and contain all atoms forming the junction. Its shape and volume depend on the tubes types, angle between their axes and history of the junction producing, and can be roughly imagined as a cylindrical-shape area of volume $V \propto (\min(D_1, D_2) + d_0)^2 (\max(D_1, D_2) + 2d_0)$, or found by numerical simulations or by experimental measuring.

In Fig. 1 a conventional diagram is given for producing the X-shape junction between two nanotubes. Certain symbols for system states S_i and interstates transitions $B_{i,j}$ are given in the bottom and top rows of the abscissa axis,

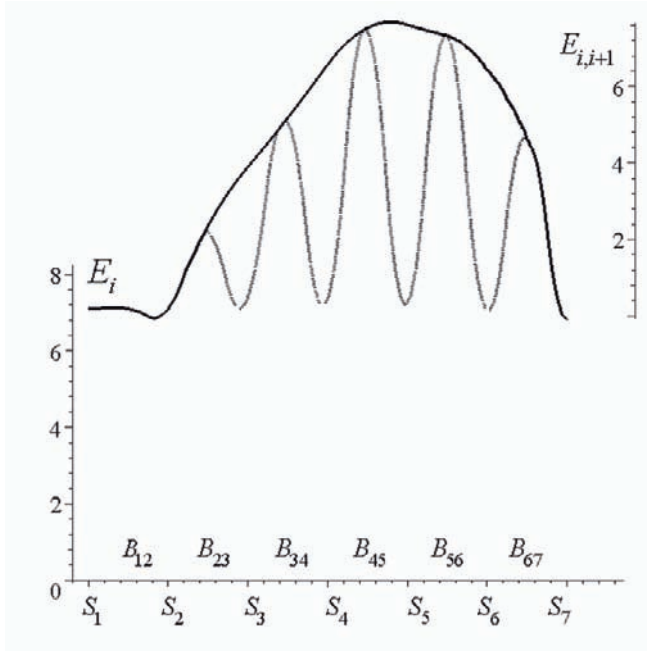


Figure 1. The diagram of physicochemical reaction for welding two single-walled CNT.

respectively. An average energy E_i^{av} of one carbon atom from the junction's area in the S_i state is presented on the left ordinate axis, and energy $E_{i,i+1}$ of the corresponding transition $B_{i,i+1}$ is given on the right ordinate axis. One carbon atom or electronic subsystem near the junction should receive necessary energy from electron beam for overcoming the barrier $E_{i,i+1}$.

Label S_1 designates a state of two free nanotubes with the distance between their walls more than between graphite layers i.e. 0.314 nm. Label S_2 designates a state, when two tubes have come nearer to each other on smaller distance, but only van der Waals interaction exists therein. Energy of system practically does not change in this state, it is reached without an irradiation, and it is considered initial at welding nanotubes.

Label S_3 designates a state of tubes with one single covalent bond, similar to bonds formed by cycloaddition [17] in fullerite during its polymerization under an electrons beam [14]. This state can be implemented due to excitation of electronic subsystem or by electron capture nearby the junction, hence $E_{23} \approx E_{ex}$, where E_{ex} is the nanotube excitation energy. It can varies within about 0-2 eV [18] in dependence on nanotube chirality, and characteristic size of area where it should take place is $d \approx (1 \div 2)d_0$. Even low-energy particles can deliver such energy into electron subsystem. We shall assume transfer of excitation on neighboring knots is unique process competing to bond formation and it occurs for the time τ . Now, the electrons beam energy can be estimated from equation

$$E_{23} \leq \Delta E = \int_0^{E_{\max}} T d\sigma(E, T) / \sigma_0, \quad \sigma_0 = \int_0^{E_{\max}} d\sigma(E, T) \quad (1)$$

where $d\sigma(E, T)$, σ_0 are differential and total cross section of scattering of an electron with energy E on carbon atom in the nanotube, and T is energy losses. Similarly, for a flux of electrons and their current the following estimates are valid

$$\Phi_3 \approx (d/d_0)^2 / \sigma_{ef}, \quad j_3 \approx \Phi_3 / \tau, \quad \sigma_{eff} = \int_{E_{23}}^{E_{\max}} d\sigma(E, T), \quad (2)$$

where σ_{ef} is a cross section of all scatterings with energy transfer $T \geq E_{23} \approx E_{ex}$. Since the total amount of such bonds can widely vary depending on the axes intersection angle, types and diameters of tubes, hence amount of the states similar to S_3 can be large enough too and then cumulative barrier for all such transitions will be a sum of all these barriers.

Label S_4 designates a state of two nanotubes when only one atom breaks off one or two bonds with its the nearest neighbours in the nanotube and forms new bonds, removing itself from the nanotube surface on a distance greater than $\sim d_0$ (so called lateral bonds). Energy barrier for this is about $\sim (1 \div 2) E_b / 3$, where E_b is atom binding energy in the nanotube. It can be easily overcome at a low-energy ion irradiation, but energy of the electron beam should be not less than 30 keV. Transitions into this and S_3 -like states can occur together. Note upon S_3 is valid concerning amount of states similar to this and cumulative energy barrier. For transition in this state estimates Eq. (1,2) are valid too at the relevant replacement of coefficients.

Label S_5 designates a state when only one atom breaks off all its bonds in the nanotube and flies off, but the system remains covalently bonded. A barrier $E_b \sim 10$ eV should be overcome for transition into S_5 , therefore energy of an electrons beam should exceed about $E_{beam} \geq 80$ keV. This estimation should be magnified still in several times since the effective cross section σ_{ef} have to be commensurable with d_0 . Transition into this state occurs by partial defragmentation of nanotubes and formation new bonds. Simultaneous removing of C_2 -dimer or larger fragment is energetically more favorable than consecutive removal of these atoms, because amount of broken off bonds is less then. It happens at fragmentation of fullerenes [20] by particle beams. Similarly previous, we suppose all removals of carbon atoms on infinity lead into S_5 -like states with a cumulative energy barrier and estimations similar Eq. (1,2). However, amount of S_5 -like states is restricted, since only N_s atoms must be removed to infinity from the junction area for producing the ideal junction.

Transitions in S_4, S_5 -states should lead to approach the nanotubes axes from an initial distance $\sim D_1 + D_2 + d_0$ up to zero. They are stages when the tubes are being locally fragmented and gradually creeping the each on the other to decrease distance between their axes due to forming new covalent bonds nearby the destroyed edges, and the surplus atoms are leaving the junction area on the single or in a composition of fragments. If the new covalent bonds are formed quickly

enough after the fragmentation then a gradual local rotation of undestroyed nanotubes parts is possible also, and it should decrease distance between their axes too.

Label S_6 designates a state when exactly N_s atoms are removed from the junction area and a nonideal junction is formed. Opposite the previous three states, this one is determined unambiguously and after its achievement the irradiation conditions should be changed. It should be adapted to rearrangement of the actual atomic configuration by removing atoms, which have formed lateral bonds, from their actual places in energetically more favorable ones. And at last, label S_7 designates the ideal junction state which is separated from the previous one by an energy barrier similar to the two previous.

Actually, the intermediate states S_3 , S_4 , S_5 , and S_6 , are not permanently implemented in the two crossed nanotubes under a continuous particles irradiation, therefore in Fig.1 these states and corresponded transitions are marked by points. However, if the irradiation would be stopped at some moment, then the system can transfer in one from these states or in some their composition, if we take into account simultaneous occurring the described above processes.

Thus, the proposed model of nanotubes welding by electron beams includes the following processes: 1) formation of covalent bonds without essential reorganization of atomic configuration; 2) a breaking off some part of bonds both with removal of atoms from junction area and without it; 3) formation of new bonds which reduce interaxial distance between tubes; 4) multiple repetition of 1-3) processes, which minimizes interaxial distance and forms a nonideal junction; 5) reorganization of actual atomic configuration to minimize the system energy and removal of surplus atoms from the junction area.

3. Results and Discussion

Numerical calculations of the proposed model parameters have been performed for welding two single-walled CNT with symmetry (10, 0). Energy barriers $E_{i,i+1}$ were obtained within the framework of semiempirical tight-binding models (ratio of the nanotube's fragment length to its diameter was equaled 4), and energy of atomic configurations was calculated within the PM3 model. *Ab-initio* calculations in the framework of the DFT have been performed also for the states S_2 and S_3 , where only the nearest neighbors were taken into account. The obtained results have coincided with each other within 10%. For armchair single-walled CNT (10, 0) we have received the following values: $B_{23} \approx 0.9$ eV, $B_{34} \approx 2.2, 4.6$ eV, depending on amount the broken off bonds in the nanotube, $B_{45} \approx 7.1$ eV, $B_{67} \approx 2.2, 4.5, 6.8$ eV, depending on amount the broken off bonds laid outside of the ideal junction surface. According to a geometrical estimation, 48 carbon atoms must be removed from the junction area for producing the X-shape junction between the tubes intercrossed under the right angle. Calculations within the PM3-model give the binding energy of a carbon atom from the junction area ~ 6.8 eV, that is appreciably less than in the free nanotubes (~ 7.3 eV) and indicates on existence of some mechanical stresses nearby of the junction.

Calculations of elastic and inelastic cross sections of electron scattering on carbon atom have been performed as in [14]. Four components optical model was used for elastic scattering and energy losses evaluations, which took into account screened Rutherford interaction, atom polarization, exchange effects, and muffin-tin approximation. Relativistic theory of scattering was used taking into account above estimations for energy of impacted electron. Threshold for radiation defect generation was established ~ 15 eV. Dielectric constants for fullerite and graphite have been used for inelastic scattering and energy losses evaluations, and both showed close results. We found, that electron can remove one carbon atom from its site in the nanotube only at energies > 80 keV, but effective cross section of this process becomes essential only at energies higher then ~ 200 keV, however remains sufficiently less then d^2 , or even a_0^2 (a_0 is the Bohr radius). We use for estimations the value $\sim 0.01a_0^2$, obtained at the energy ~ 0.2 MeV, and it leads to the low limit for the electrons flux $\Phi \geq 6 \cdot 10^{17} \text{ sm}^{-2}$. Lifetime of nanotubes excited electrons is about $\sim 10^{-14} - 10^{-13} \text{ s}$ [20] it is caused by the electron-electron interaction, and does not compete to new covalent bonds creation. Since cooling of the junction area due to lattice heat conductivity can slowed this process, we took into account it and obtain an estimation of electron beam current $j \approx 10^{25} \text{ sm}^{-2}\text{s}^{-1}$. Nowadays such currents can be produced only by using focused beams.

4. Conclusion

The carried out calculations and estimations give results comparable with calculations of other authors and available experimental data [2,7]. According to them, the welding of nanotubes seemingly occurs as a result of simultaneous action of several processes: a local fragmentation of tubes; creeping of the tubes along the destroyed bonds or/and their rotation around them leading to approaching of their axes; formation of new covalent bonds; removal of surplus atoms from the junction area and rearrangement of the lateral bonds. Parameters of an electrons beam which are necessary for producing a heterojunction by welding of two single-walled CNT can be calculated by using the proposed model.

Acknowledgements

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THEORETICAL STUDY AND EXPERIMENTAL INVESTIGATION OF HYDROGEN ABSORPTION BY CARBON NANOMATERIALS

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Abstract. Investigations of hydrogen adsorption in different carbon nanomaterials obtained from carbon-helium plasma were carried out. Five types of samples were investigated: fullerene-containing soot collected from chamber walls and from chamber outlet, fullerene mixture, thermolysis residue, and graphitized in plasma Al_2O_3 . It was found that the soot from chamber outlet containing more than 40% of single-wall carbon nanotubes (SWCNT) was the best hydrogen adsorbent. This sample adsorbed 0.92%wt. of hydrogen at 77K and 10^7 Pa. Also theoretical study of hydrogen adsorption on SWNT inner and outer surfaces was carried out with accounting of van der Waals interaction. It was determined that adsorption on the outer nanotube surface was less efficient than on the inner surface because of reduced effective potential of attraction of H_2 molecule to a carbon wall. Our theoretical study just as our experimental investigation had shown that efficient hydrogen storage by carbon materials can not be solved on the base of physical sorption mechanism only.

Keywords: hydrogen sorption, carbon nanotube, fullerene

1. Introduction

There are many papers containing contradictive information about quantities of hydrogen stored by carbon materials, obtained by different authors [1-3]. It can be induced by differences in material structure, contents or defects, which lead to the large discrepancy of stored hydrogen value. In this paper we present the experimental results of hydrogen sorption investigations by different carbon materials formed in carbon-helium plasma at atmospheric pressure. These results are in good agreement with the results of our theoretical studying.

2. Experimental setup

Our developed setup for measuring of adsorbed hydrogen quantity (Fig. 1) allows to investigate rapidly the hydrogen adsorption at temperatures of 77-1273 K and pressures up to $1.5 \cdot 10^7$ Pa.

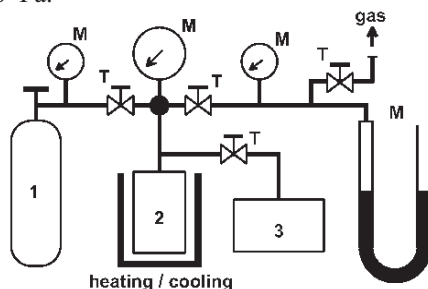


Figure 1. Scheme of setup for investigation of hydrogen sorption: 1 –vessel with hydrogen; 2 – chamber for investigated sample; 3 – vacuum pump; M – manometers; T – taps.

Investigation of hydrogen sorption by different materials was carried out by the next technique. Every sample was heated up to 773 K (500°C) with simultaneous gas pump-down to 0.013 Pa (10^{-4} Torr). Evacuation was carried out by the pre- and diffusion pumps through liquid nitrogen trap. Then vacuum pumps were turned off and hydrogen was let in at pressure of $1.0 \cdot 10^7$ Pa (100 atm). A sample was cooled down to 77 K at invariable hydrogen pressure and exposed 20 minutes at this pressure. To register desorbed hydrogen the sample was smoothly heated and the volume of the desorbed gas was registered at normal pressure by U-shaped manometer. Maximal heating temperature varied for different samples because of their different thermal stability.

3. Experimental results

Investigations of absorption properties of the sample series: thermolysis residue (T), fullerene soot from chamber walls (S2), fullerene soot collected at chamber outlet (S1), and fullerenes (F) were carried out. Also the investigation of hydrogen sorption by graphitized sorbent Al_2O_3 (A) obtained by original plasma technique [6] was carried out.

All samples were obtained in the setup for fullerene synthesis by the technique described earlier [4-5]. Novelty of this technique was that materials were produced in plasma-chemical reactor without air access and they shifted to the chamber for the sample investigation, see Fig. 1.

The obtained temperature dependencies had shown that the quantity of desorbed hydrogen is increased with increasing of the temperature for all carbon samples (Fig. 2). Maximal hydrogen content (0.92 % wt.) was registered for the soot collected at the outlet surface of the fullerene synthesis chamber. By the method of electron microscopy it was detected that this sample contained 9% of fullerenes and more than 40% of single-wall carbon nanotubes (SWCNT).

Our experimental results are in a good agreement with results of other authors [3] showed that nanotubes have the best hydrogen sorption ability among known carbon nanostructures.

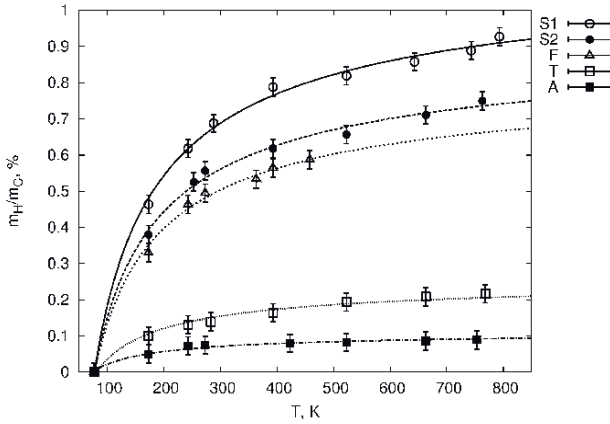


Figure 2. Temperature dependence of desorbed hydrogen mass from different samples: S1 – fullerene soot collected at chamber outlet surface, S2 – fullerene soot collected from chamber walls, F – fullerenes, T – thermolysis residue, A – graphitized Al_2O_3 .

4. Theoretical model of hydrogen adsorption on nanotube surface

To simulate hydrogen adsorption by single wall nanotubes the method was developed [7] which allows to take into account quantum and thermal effects at light molecules adsorption. This method uses interaction potential of adsorbed molecules with van der Waals force accounting. This method has high efficiency and can be used for adsorption value calculation in systems with any quantity of atoms at any temperature. The method is based on solving of the Shrodinger equation for the adsorbed molecule which move in potential produced by circumjacent hydrogen molecules and nanotube wall atoms:

$$\left(-\frac{\partial^2}{\partial r^2} + V(r) \right) \Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (1)$$

$$V(r) = \sum_i V(r - R_i)$$

We assumed that for minimum energy the carbon atoms in nanotube wall hydrogen molecules should be placed with periodicity in lattice points. Because of carbon atoms periodicity is the hexagonal lattice the hydrogen molecules should be placed in points of the same lattice but with a parameter a determining the density of adsorbed H_2 molecules (Fig. 3).

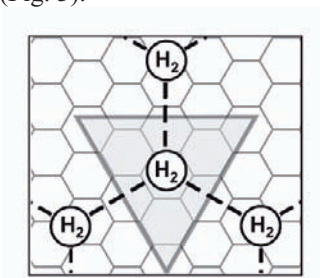


Figure 3. Unit cell projection (gray triangle) of hydrogen molecule on nanotube surface and its nearest neighbors.

We had chosen unit cell for hydrogen molecule movement as a triangular pyramid (with the height enough for the hydrogen molecule localization) with projection on nanotube surface in the form of equilateral triangle (gray triangle on Fig. 3) with obvious boundary condition: $\Psi_i(r)|_{\text{boundary}} = 0$. Also we assumed that all hydrogen molecules located at an equal height $R_{\min}$ from nanotube surface (inside or outside). $R_{\min}$ was determined from condition of the system energy minimum toward the height of molecules location above the surface: $dE(R)/dR|_{R=R_{\min}} = 0$.

In the calculations the hydrogen molecules interaction potential $V(r)$ in the Silvera-Goldman form [8] was used, which good describes experimental data of molecules H_2 interaction including weak van der Waals H_2 molecule interaction. Interaction potential between hydrogen molecule and carbon atoms was accounted in the same way. Because of importance of taking into account van der Waals interaction having correlational nature we could not use any quantum chemical programs for ab initio calculations because this interaction does not considered in them.

After Shrodinger equation solving the probability $\rho(r)$ of H_2 molecule presence in point r determined quantum-mechanically as $\rho(r) = \sum_i \Psi_i^2(r) \Theta_i$ where $\Theta_i = Z^{-1} \exp(-\varepsilon_i / kT)$ is the occupation factor of the i -th energy level.

In the model the fact that at temperature $T > 0$ the particle (H_2 molecule) can jump to exited levels i and change by that the distribution $\rho(r)$ and the average energy of a particle $E_{\text{tot}}(a, T) = \sum_i \varepsilon_i \Theta_i$ was taken into account. Using the Gibbs distribution for the energy level occupation Θ_i at given temperature T , one can calculate $E_{\text{tot}}(a, T)$ and other quantities depended on the temperature T and pressure P in the system.

In the Free energy $F(a, T)$ calculation phonon contribution $F_{ph}(a, T)$ was taken into account which allowed taking into account correlations in positions of neighbouring adsorbed molecules:

$$\begin{aligned} F(a, T) &= F_0(a, T) + F_{ph}(a, T), \\ F_{ph}(a, T) &= -kT \log Z_{ph}, \\ Z_{ph} &= \prod_i e^{-\hbar\omega_i / kT} / (1 - e^{-\hbar\omega_i / kT}) \end{aligned} \quad (2)$$

Phonon vibration spectrum was determined from force constant k which was determined from dependence of the calculated molecule average energy on volume ($\approx a^3$), i.e. from compressibility $k \cong \partial^2 E_{\text{tot}}(a, T) / \partial a^2$. The pressure in the system was determined conventionally as $P(a, T) = -\partial F(a, T) / \partial V$. One can determine the lattice constant $a(T)$ for every value of (P, T) by numerical inversion of the dependence $P(a, T) \Rightarrow a(P, T)$.

Equilibrium hydrogen concentration $m(P, T)$ was determined from the lattice constant $a(P, T)$ of hydrogen unit cell at minimum value of the Gibbs thermodynamical potential $G(P, T) = F(P, T) + PV$.

At every chosen values of P and T we determined the lattice constant a and hence the value of $m(P, T)$. It was found this potential can have several minima at given pressure P and temperature T , therefore phase transitions of adsorbed hydrogen density $m(P, T)$ are possible in this system.

5. Theoretical results

On the base of this approach thermodynamics of hydrogen absorbed outside and inside the (10,10) and the (20,20) single-wall carbon nanotubes with diameters 13.56 Å and 27.13 Å, respectively, was calculated. The dependencies of free energy F and thermodynamical potential H on applied pressure P and temperature T were calculated. The dependencies of content of hydrogen adsorbed on nanotubes $m(P, T)$ surface on pressure and temperature were calculated from these data. For the first time the dependencies of $m(P, T)$ with accounting of quantum effects and van der Waals forces were calculated.

Our calculations had shown that density of adsorbed hydrogen on SWCNT surface can be changed by jump, i.e. have phase transition. At that density of adsorbed hydrogen increased at pressure increase and temperature decrease.

It was determined that adsorption on the outer nanotube surface was less efficient than on the inner surface because of reduced effective attractive potential affecting to the H_2 molecule from atoms of a carbon wall (Fig. 4).

Adsorption also was decreased at SWCNT diameter increased over reducing of the effective attraction of H_2 molecules to SWCNT surface. The calculations had shown that the maximum total sorption at both sides of nanotube walls does not exceeded 3% at pressures up to $5 \cdot 10^7$ Pa.

Further we studied ability of chemical hydrogen adsorption on a SWCNT surface by hydrogen molecule dissociation to atoms. With the help of LDA calculations it was found that energy of thermal dissociation of H_2 molecule changed insignificantly at molecule movement to SWCNT or fullerene surface. This energy had a value about 6 eV. Therefore the probability of hydrogen chemisorption on SWCNT surface is very low at common temperatures without a catalyst influence.

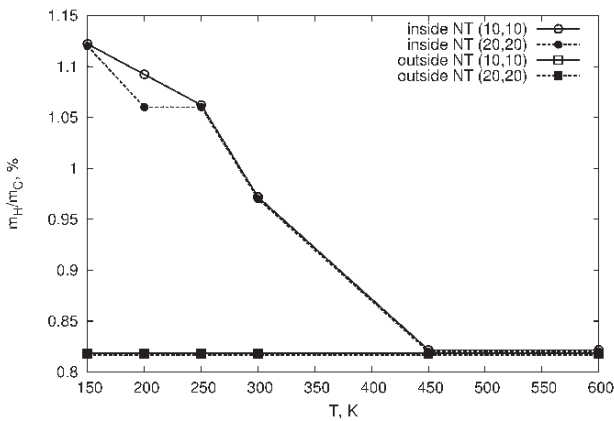


Figure 4. Calculated temperature dependence of adsorbed hydrogen mass at 10^5 Pa.

6. Conclusion

Our theoretical study of hydrogen adsorption on SWCNT surfaces with accounting of quantum, thermal effects and van der Waals interaction just as our experimental investigation allow to confirm the conclusion that efficient hydrogen storage by carbon materials can not be solved on the base of physical sorption mechanism only. In the future we plan to study mechanisms of hydrogen chemical sorption and to search effective catalysts of this process.

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RADIATION INDUCED PHENOMENA ON ELECTRONIC AND PROTONIC CONDUCTIONS OF COMPACT HYDRIDE-ELECTROLYTE FUEL CELL

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Abstract. Electrical and protonic properties of Ytterbium-doped perovskite-type strontium-cerium oxide ceramics ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$) including hydrogen (H), implanted with 10 keV H_2^+ ions into zirconium film deposited on the one side only of the specimen, were investigated under a fission reactor irradiation. It was found that the radiation induced conductivity (RIC) for the specimen with H at 0.5 kGy/s was higher by about two orders of magnitude than the base conductivity without radiation at 0 Gy/s, and higher than that without H. The RIC is attributed to the electronic excitation as well as enhanced diffusion of hydrogen due to ionizing irradiation. Also, the RIC with H greatly depended on the irradiation temperature and hardly change with the fast neutron fluence, while that without H reduced with increasing the fluence. The fluence dependence on the radiation enhanced diffusion of H shows that the radiation induced defects, produced by neutron collisions, and the radiolysis have no influence on the protonic conduction.

Keywords: Compact fuel cell; Proton conductive oxide; Radiation induced conductivity; Radiation enhanced diffusion

1. Introduction

Development of compact fuel cells, created by combining proton conductive perovskite-type oxide ceramics with metal-hydride materials, has been already proposed [1]. Our group expects that the compact fuel cells can be utilized under radiation environments such as fission and fusion reactors or cosmic [2]. Therefore, it is very important to understand behaviors of electron and proton conductions under radiation environments.

In the present study, the electrical conductivity of the ceramics was measured in-situ at irradiation temperatures below 473 K (first cycle: 29 reactor full power days) and 673 K (second cycle : 27 reactor full power days) under fission reactor irradiation, and radiation induced phenomena on electronic and protonic conductions in the ceramics are discussed.

2. Experimental

The specimen used in the present experiments was $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ which had orthorhombic structure and exhibited high protonic conductivity under a hydrogen-containing atmosphere at temperatures above 573 K [3]. Dimension of the specimen was $\phi 8$ mm diameter and 1 mm thick. After etching on the surface of specimen by Ar^+ ion sputtering in a high vacuum, zirconium metal (Zr) of 1.0 μm thick was deposited on one side of the specimen using an electron beam-sputtering device, and hydrogen atoms were implanted into the Zr film with 10 keV H_2^+ ions at 473 K. The fluence was about 5.0×10^{21} H/m^2 . In order to make hydrogen atoms transported by chemical reaction easily, and zirconium oxide (ZrO_2) was deposited on another side of the specimen. Moreover, two platinum electrodes of 3 mm diameter and 1 mm thick were connected on both sides of the specimen with silver conductive paints. The specimens with and without H were accommodated in a fixture (sub capsule) made of copper and alumina, used as a guard ring geometry and were installed in a specially designed irradiation rig. The irradiation rig was filled with helium gas at a pressure of 1.0×10^5 Pa and inserted to the vertical direction to the ground in a fission reactor core of Japan Materials Testing Reactor (JMTR) in oarai research establishment of Japan Atomic Energy Research Institute (JAERI).

Electrical conductivity measurements were carried out by recording DC-currents when applying DC-voltages of ± 30 V under the reactor irradiation [4]. The DC electric field was disconnected during irradiation, except for the short times needed for the measurements. Magnesia insulating electrical triaxial cables with 1.6 mm diameter were used to carry the electrical signals. The inner conductor and outer sheath materials were made from nickel and stainless steel, respectively. The length of the cable was about 10 m [5].

The reactor power was raised sequentially up to 50 MW. When the reactor power reached 50 MW, the irradiation temperatures for the specimens with and without H increased up to 401 and 473 K for the first cycle, respectively, and 519 and 673 K for the second cycle, respectively, adjusted by introducing or evacuating He gas in the irradiation rig, in order to change the heat conduction. The ionizing dose rate, due to mainly gamma-ray, for the specimens with and without H were 0.5 and 1.8 kGy/s, respectively, at the reactor full power of 50 MW. The fast ($E > 1.0$ MeV) and thermal ($E < 0.683$ eV) neutron fluxes for the specimens with and without H were 2.73×10^{16} and 1.26×10^{17} $\text{n}/\text{m}^2\text{s}$, respectively, and 4.05×10^{17} and 1.34×10^{18} $\text{n}/\text{m}^2\text{s}$, respectively. The reactor full power days at first and second cycles were 29 and 27 days, respectively. The resultant ionization doses and the fast neutron fluences for the specimens with and without H were 2.3×10^3 and 8.4×10^3 MGy and about 1.31×10^{23} and 6.02×10^{23} n/m^2 , respectively.

3. Experimental results and discussion

Figures 1(a) and (b) show relations between the currents measured and the voltages applied for the specimens with and without H, respectively, at several ionizing dose rates for the first cycle. The currents at the applied voltage increased as the ionizing dose rate increased. Moreover, the irradiation temperature was also gone up to 473 K by gamma-heating. The increment of the irradiation temperature has a little influence on the increment of the current. However, it is, for the temperature below 473 K, much lower than the radiation effects.

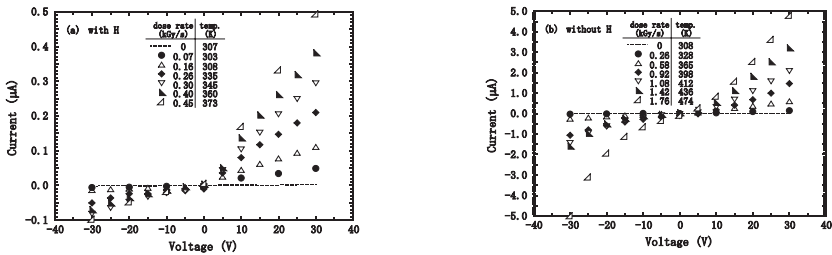


Figure 1. Relation between the measured current and the applied voltage for SrCe_{0.95}Yb_{0.05}O_{3-δ} specimens (a) with and (b) without H during reactor irradiation.

The current for the specimen with H is proportional to the applied voltage and is asymmetric at positive and negative voltages. The difference may be possibly due to trapping of H at the cathode electrode by hydrogen migration. On the other hand, the current for the specimen without H exponentially increased with increasing the applied voltage.

Figures 2(a) and (b) show radiation induced conductivity (RIC) for the specimens with and without H as a function of ionizing dose rate at the first and second cycles, which were calculated using Ohm's law from the experimental data between from 0 to +10 V and the specimen volume. The conductivity increased with the increase of the ionizing dose rate. The values at the ionizing dose rate of 0.5 kGy/s became higher by two orders of magnitude than that without radiation, namely it is 0 Gy/s. The RIC with H is higher compared with that without H. Therefore, the RIC may be caused by electronic excitation as well as enhanced diffusion of H due to ionization irradiation. After irradiation for 29 reactor full power days, the second reactor irradiation experiment was carried out for 27 days. The RIC with H at first cycle is almost same as that at second cycle. The RIC without H at several ionizing dose rate decreased by about one order of magnitude.

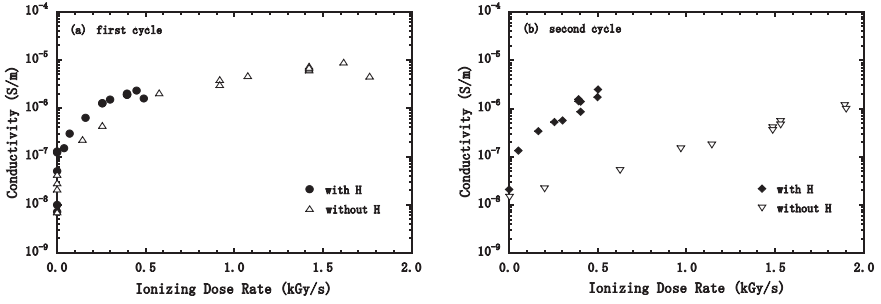


Figure 2. Conductivities for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ specimens with and without H as a function of ionizing dose rate at (a) first and (b) second cycles.

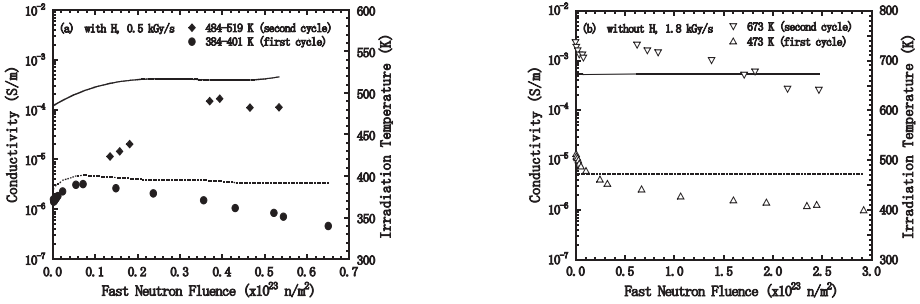


Figure 3. Fast neutron fluence dependence of conductivities for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ specimens (a) with H at 384-401 and 484-519 K and (b) without H at 473 and 673 K, respectively.

Figures 3(a) and (b) show fast neutron fluence dependence of conductivities for the specimens (a) with and (b) without H at ionizing dose rates of 0.5 and 1.8 Gy/s, respectively. The irradiation temperatures for the specimens with and without H were 384-401 and 473 K at the first cycle and 484-519 and 673 K at the second cycle. It was found that the RIC increased with raising the irradiation temperature. Particularly, the RIC with H greatly corresponds to the change of the irradiation temperature. On the other hand, the RIC without H quickly decreased at the initial fluence and hereafter gradually as the fast neutron fluence increased, even if the irradiation temperature was constant.

These results indicate that the radiation induced defects such as some point defects, dislocations and lattice distortions have no influence on the protonic conduction. However, the electronic conduction is modified by sub-band annihilation in gap between valence and conduction bands after neutron irradiation [2, 6, 7].

4. Summary

The RIC of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ specimens with and without H was observed under fission reactor irradiation. The RIC for the both of them increased with increasing ionizing dose rate, and those with H at the maximum ionizing dose rate of 0.5 kGy/s, by 50 MW reactor power, and without H at 1.8 kGy/s were higher by about two and three, respectively, orders of magnitude than the base conductivity without radiation at 0 MW. The RIC with H in the dose rate range of 0.5 kGy/s was higher than that without H. The result may show that the RIC is caused by electronic excitation as well as enhanced diffusion of hydrogen due to gamma irradiation. After irradiation for 27 reactor full power days, the RIC for second cycle was measured again. The RIC with H was almost same as the result for the first cycle, while that without H reduced lower by about one order of magnitude. The radiation defects, produced by the neutron fluence of about 10^{23} n/m^2 , may show no changes for the protonic conduction but the electronic one.

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DEFECTOSCOPY AND PERSPECTIVES RELATED TO METALLIC MATERIALS ADOPTABLE IN HYDROGEN STORAGE PRESSURE TANKS PRODUCTION

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Abstract. The present work deals with major technical items related to defectoscopy of metallic materials - in particular, welded joints - which can be considered as constitutive for H-storage high pressure tanks: such vessels must be corrosion and pressure-resistant, especially in order to avoid any infiltration by light H-atoms and, in general, H-embrittlement and Stress Corrosion Cracking (SCC) phenomena.

Various investigations have been carried out on steels and aluminium alloys, by adopting different techniques, in particular radiography, microanalysis and Small Angle Neutron Scattering (SANS).

The main results are reported, which connect development and testing of prototype Hydrogen storage tanks with the requirement of a study in depth of the involved constitutive materials defectoscopy and microstructural characteristics, in order to better understand their behaviour and assess their suitability.

Keywords: Hydrogen storage; Steels; Aluminium alloys; Radiography; SANS; defects.

1. Introduction

Hydrogen represents, currently, the most potent fuel going - packing almost three times gasoline's energy -, and its employment is considered able to reduce carbon dioxide emissions till ~60% compared with diesel based systems.

A pre-condition for Hydrogen use is to solve the problem of its storage and circulation under acceptable conditions, taking into account also the costs of such operations. Hydrogen can be stored in the form of gas, cryogenic liquid or adsorbed gas in solid materials. The most ordinary type of storage involves confining the

compressed gas in secure tanks, with a pressures range of $\sim 200\text{--}800$ bars and an estimated averages size of fixed tanks (distribution stations) of $\sim 1 \cdot 10^4 \text{ m}^3$. Conventional storage, such as compressed gas cylinders and liquid gas in cryogenic tanks, should be made stronger, lighter and more economical. The ideal material for a high pressure vessel should have an elevated tensile strength - not essentially isotropic -, a low density, and should not interact with Hydrogen or allow Hydrogen diffusion. The majority of pressure vessels have used, so far, austenitic stainless steel, Al alloys or Cu, which are considered basically resistant to Hydrogen effects at ambient temperatures [1].

Hydrogen is frequently related with mechanical properties degradation and failure, in particular corrosion defects. The diffusion of the atomic Hydrogen (H^+) from the H_2 molecule against the tanks constitutive plate can generate cracks similarly to Hydrogen Induced Cracking (HIC), especially to the presence of residual stresses (RS), and high Hydrogen motilities have been revealed at ambient temperatures in metallic and nano-structured materials [2]. Cracking, blistering and embrittlement can also be caused by dissolved H [3].

Defectoscopy and characterization of metallic materials suitable for Hydrogen storage tanks production plays a decisive role in the debugging of new vessels, giving a crucial support to advance safety and durability. The application of any material, in fact, requires more knowledge about its behaviour under high pressure, aggressive environment and weld conditions. Mechanical properties, such as creep resistance and joints ageing, are strongly dependent on nanostructure (precipitates, pores and dislocations groups) formed in the metal. A not uniform degradation of the material leads to extremely fast development of cracks and crucial reduction of welded joint's lifetime. Crack-like surface braking defects, in particular, are considered as products age, since with load and environment the risk of failure on the surface increases. Crack starting and development is nearly unpredictable, since it depends in wide measure from the RS extent and distribution inside the material (especially in the weld bead and in its surrounding zones). Stress concentration near the precipitates is also responsible of enhancing the nucleation rate of cavities [4]. Either weld deposits or HAZ can present creep proprieties significantly differing from those of base materials, due to the complexity of welding process, which involves alloying effects, heat treatment, phase transformation, solidification and RS [5].

The above mentioned defects can interact with the surface, limiting the detection capability. NDT methods, in this case, are required by standards such as the KTA guidelines for pressurized vessels.

A development of welding processes is also essential to obtain quality assurance improvement and safety enhancement of the involved welded joints. Recent investigations of welds have shown the benefits related to the employment of neutron techniques, to achieve substantial information on structural peculiarities that cannot be found by using other means [6]. Neutrons techniques are more and more becoming acknowledged as a valuable tool for structural-integrity assessment of industrial components and advanced materials development [7]. SANS method, in particular, giving rich information on metals nanostructures can be applied for the investigation of structural peculiarities of welded joints, in order to predict joint quality changes at very early stage defects' growing [8]. A welded joint SANS scan enables obtaining the data on nanoscopic characteristics inside the joints, assuming

possible local deviations in technology, composition, etc. [6]. SANS-experiments have elucidated, for instance, subtle structural changes in embrittled steel, enabling to define the main structural elements (defects) to be monitorized in the material to forecast their proprieties and equipment safety [9].

The feasibility of adopting neutron diffraction to measure RS in welded joints, on the other hand, is largely shown by various experiments carried out in different neutron sources. The adoption of neutron techniques enables also:

- To investigate the control factors of welded component's fatigue behaviour, and use the analytical methods for estimating the total fatigue life of welds subjected to variable-amplitude loading histories and surface treatments, in order to find some possible methods to improve the fatigue strength.
- To apply the probabilistic methods to estimate micro-cracks possible nucleation within a joint metal (fatigue damage processes).

2. Experimental, results and discussion

Various investigations have been carried out on steels and aluminium alloys, in particular on the following materials: AISI 316, AISI 316 L, AISI 304, Fe 410, P-Al Mg 4,4 UNI 5452, and 08H18N10T austenite stainless steel. The investigated samples belong to base plates as welded or to vessels plates before and after exercise.

The adopted methods were: x-ray radiography (RT-X), especially concerning circumferential and longitudinal joints; magnetic particle testing (MT); ultrasonics (UT); tensile and cold-bend test; macroscopic sections; hardness test; metallographic examinations; microanalysis (EDS); SANS.

The main defects revealed have been: cracks and micro-cracks; cavity inclusions, due to the welding process or to the quality of the adopted gas; discontinuity of the weld bead; weld sticking; segregation lines of inter-metallic and not-metallic (silicates, oxides, etc.) compounds, in the thickness centre of welded plates, imputable to the materials quality.

RT-X highlighted weld and base material defects such as SCC, porosity, shallowing around edge of weld seam, slag and gas inclusions. Figure 1 shows, e. g., the presence of a longitudinal crack near the weld of an AISI 316 vessel after exercise, while Figure 2 represents passing cracks transversal to the weld bead of a Fe 410 vessel after exercise.

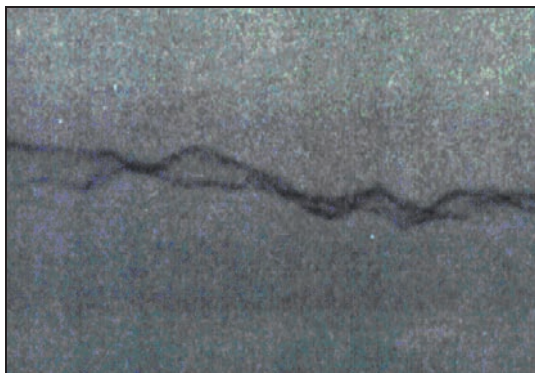


Figure 1. Longitudinal crack near the weld of an AISI 316 vessel after exercise.

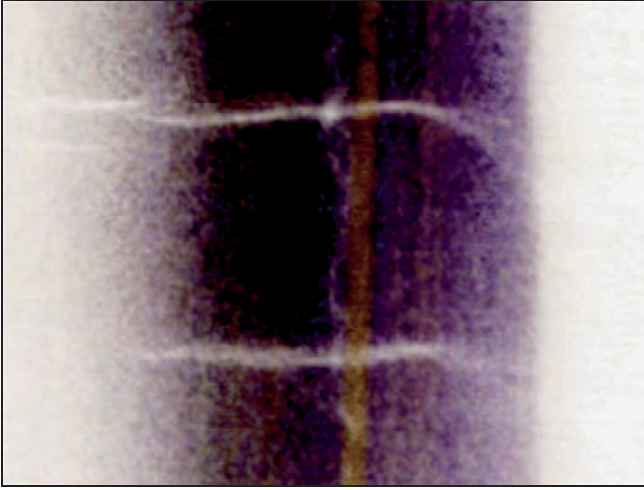


Figure 2. Passing cracks transversal to the weld bead of a Fe 410 vessel after exercise.

Figure 3 (submerged arc welded AISI 304 plate) and Figure 4 (P-Al Mg 4,4 UNI 5452 MIG welded plate), both belonging to new vessels, show the presence of porosity (gas bubbles) imputable to a discontinuous welding speed and to high values of process electrical parameters.



Figure 3. Porosity in a submerged arc welded AISI 304 plate of a new vessel.



Figure 4. Porosity in a MIG welded P-Al Mg 4,4 UNI 5452 plate of a new vessel.

The P-Al Mg 4,4 UNI 5452 MIG welded plate of a new vessel represented in Figure 5 shows low penetration defects imputable to a not correct plate edges approach.

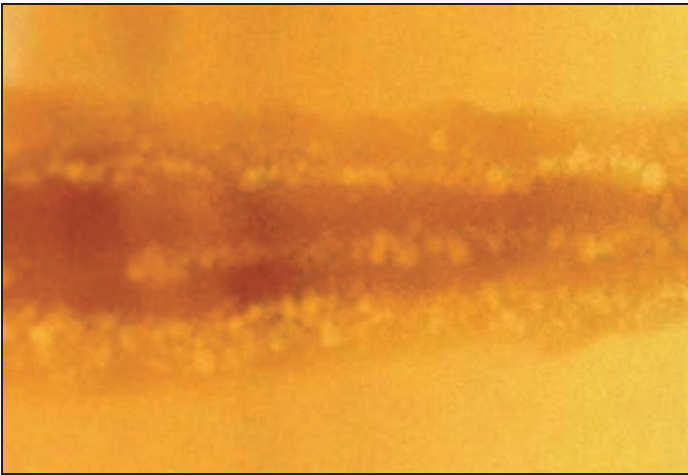


Figure 5. Low penetration defects in a MIG welded P-Al Mg 4,4 UNI 5452 plate of a new vessel.

MT underlined porosity, crater cracks, SCC and shallowing, while UT, performed by using pulse echo with dual probe, highlighted a thickness reduction (≤ 2.5 mm) only in correspondence of surface corrosion areas of vessels plates after exercise. Tensile, cold-bend and hardness test confirmed, in general, the values specified by the norms for each investigated material. Nevertheless, it should be underlined that too high ultimate tensile strength can help the appearance of material ageing phenomena.

Macroscopic sections have shown oxide layers and corrosion traces in correspondence of circumferential overlap joints with flanging of used vessels. The observance of a max distance between overlapped plates is important, in this case, to avoid such defects. Concerning welding process electrical parameters, moreover, higher values than the specified ones - sometimes adopted to increase welding speed - enlarge the dendrite grain in the melted zone, enhancing RS and reducing corrosion resistance.

Metallographic tests and EDS performed on vessels plates after exercise have shown mainly micro-cracks and pits in the HAZ, and circumferential passing cracks in the base material near the welds.

Figure 6 shows an inter-trans-granular branched crack from inside surface of an AISI 316L vessel bottom, while Figure 7 shows the presence of a micro-crack on a Fe 410 tank internal surface, in correspondence of the circumferential weld bead overlapped with the mantle longitudinal weld. Both figures are referred to materials after exercise; the represented cracks are due to the infiltration of aggressive elements and to the presence of RS produced by both welding processes.

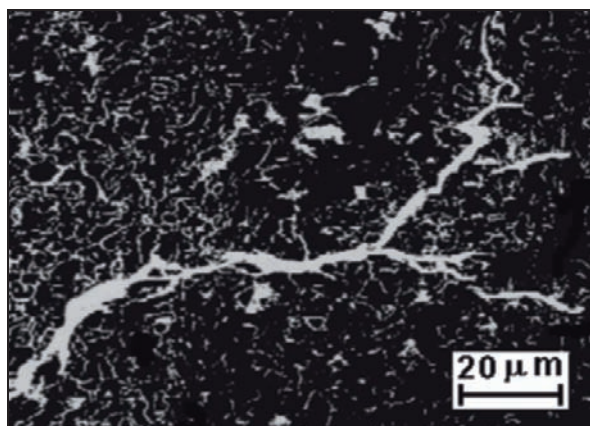


Figure 6. Inter-trans-granular branched crack from inside surface of an AISI 316L vessel bottom.

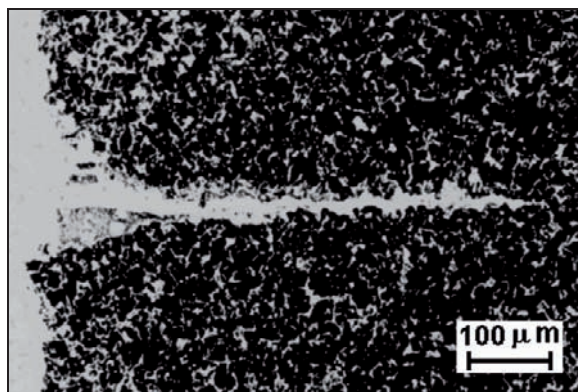


Figure 7. Micro-crack on a Fe 410 vessel internal surface.

A SANS investigation is finally reported, carried out on a sample cut out from a plate of base metal (100 mm, 08H18N10T austenite stainless steel, SU standard) and welded by the wire (3 mm in diameter, steel 04H19N18M3) in electric arc using flux 48-OF-6.

The base metal and the welded joint have been thermally treated, cooling down in water from the initial temperature 1050°C. The welded joint has been scanned by a thin neutron beam to obtain the SANS data for base and welded metal. The cross sections showed three fractions of particles with gyration radii: $R_{g1} \sim 20$ nm, $R_{g2} \sim 9$ nm and $R_{g3} \leq 1$ nm (point like defects). The amount of these defects in base metal was larger by factor 5, as compared to welded metal (see Fig. 8).

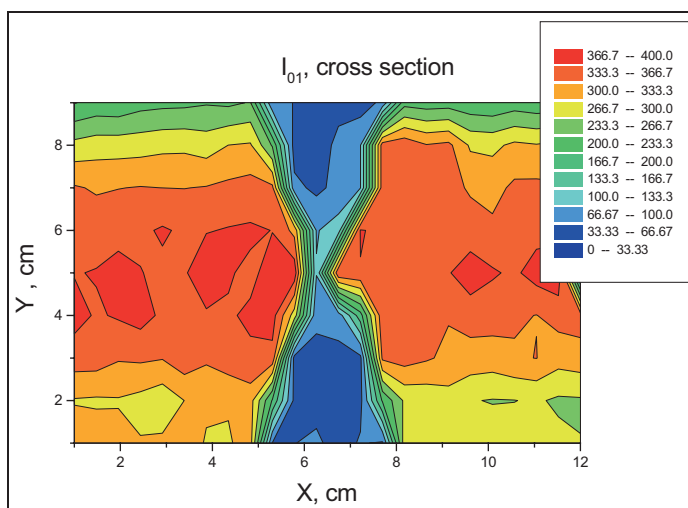


Figure 8. SANS-scan over 08H18N10T austenite stainless steel welded and base metal: forward cross section I_{01} (per cm³) for large defects $\sim R_{g1} \sim 20$ nm, colour scale in units of cm⁻¹. Right and left pieces are base metal and joint metal in between (coupled triangles).

The observed scattering is attributed to Cr_{23}C_6 precipitates, and their content in base metal ($C_B=0.1\%$ vol.) corresponds to the amount of carbon ($C_{CB}=0.05\%$ wt) that is close to its total concentration in steel ($C_{Cmax}=0.07\%$ wt.). The concentration of precipitates in welded metal, on the other hand, is lower ($C_W=0.02\%$ vol.), and only a small amount of carbon (0.01% wt.) is precipitated [6].

A SANS investigation of P91 martensitic steel (9Cr1MoVNb) samples obtained by cutting 24" pipes (thickness=14 mm) is currently being considered. The test system contains longitudinal welds in straight parts and double axial welds in the connections. The system will be submitted to 3000-8000 hours accelerated creep tests, i. e. to 7000 start cycles after 100000 hours (max. gradient $<10^\circ\text{C}/\text{min.}$). The test temperature is $\sim 545\text{-}625^\circ\text{C}$, the test pressure is $\sim 50\text{bar}$. SANS analysis with the variation of mechanical loading can supply information on the nanoscopic and microscopic defects progress: from dislocations to their groups and to voids and cracks. The thermal treatment will produce the growth of some inclusions (precipitates), allowing to obtain also their characteristics - number and size distribution - by knowing the chemical nature of precipitates - e.g. carbides Cr_6C_{23} , etc. A sample will be investigated from the original material, other samples - including welds - after the test, in order to check the microstructural changes (nano-defects, voids etc). The comparison of SANS cross sections for fresh-prepared and aged samples will provide the data on the size concentration and distribution of new defects induced by mechanical treatment. The main aim of the mentioned creep tests is to determine, before reaching the 30000 operative hours, the accelerated data which help to predict the stress/strain level at 100000 hours. A second aim could be to contribute to the elaboration of constitutive equations in order to perform interpretative analyses of some effects such as temperature, stress and strain, which is a correct step for considering temperature, hold-time, relations with primary/secondary phases of creep, etc. The same equation will represent the strain as a function of temperature and stresses, also taking into account the voids changes after the thermal treatment. Results are expected to supply very useful information for technologies of vessel and pipeline industry, also related with Hydrogen storage design.

RS knowledge in the involved welds is a relevant factor to take into account. Although numerical modelling is a powerful instrument for RS calculation, validation with reference to experimental results is essential. Neutron diffraction, in this case, represents a valuable solution in order to perform internal RS measurements, offering significant improvements in welding joints assessment and their behaviour in practice, in order to better characterise metallic materials adoptable in Hydrogen storage tanks production. Various RS measurements carried out on welded joints [6] can be mentioned, which are referable also to the present work.

Planar tomography could be complementarily adopted to indicate cracks and determine their depth propagation with high resolution, while time of flight diffraction (TOFD) has been considered not suitable as a surface crack inspection. Ultrasonic equipment such as phased array technique, on the other hand, allows complete weld inspections, improving, for instance, the separation between back wall and defect indication [10].

A special gadget is mentioned, finally, which has been studied to improve depth determination of very small thin defects - such as cracks and inclusions - mainly in thick welded components by RT-X [11].

3. Conclusions

The safety of pressure vessels is a concern, particularly in inhabited areas. Development and testing of prototype Hydrogen storage tanks should be connected with a study in depth of defectoscopy and microstructural characteristics of the involved constitutive materials, in order to understand more deeply their behaviour and assess their suitability.

Risk evaluation programmes exist, for pressure vessels, which take into account European Directives [12]; the risk factor - related to material brittleness and embrittlement, corrosion effects and localised stresses - is elevated and requires the adoption of rigorous safety measures. The manufacture and control procedures – including welding parameters and structural solutions - should be, in this case, more accurate and devoted to avoid the described defects.

Modern three layers pressure vessels are under study, which consist of a stress-bearing component - an inner polymer liner over-wrapped with a carbon-fibre composite - and an outer aramid-material layer, mechanical and corrosion damage resistant [1]. A system for the gaseous hydrogen storage at room temperature has also been designed, adopting a definite number of linked cylindrical pressure vessels [13].

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ELECTROPHYSICAL PROPERTIES OF THE NANOCARBON MATERIALS

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Abstract. The model for describing the electrical conductivity of nanocarbon material, consisting of the particles of disordered carbon, carbon nanotubes and the ordered carbon phase is proposed.

Keywords: Carbon nanoparticles; Arc-discharge; Modeling; Electrical properties

1. Introduction

Nanocarbon material (NCM), containing both the ordered carbon structures (carbon nanotubes (CNT), the particles of nanographite) and the particles of the disordered carbon phase, is known to be promising for using as elements of the nanodimensional devices and as fillers, for example, of lithium batteries. Structure and phase composition of NCM depend essentially on the methods of their obtaining and the regimes of the subsequent temperature and chemical treatment. Therefore, finding the correlation between the structural and phase composition and transport properties of NCM as well the description of the mechanisms of their conductivity are the important problems.

This work presents the model of electrical conductivity of NCM of different phase composition, structure and morphology.

2. Model

As it was shown recently [1-3], NCM is the complex heterogeneous system, which contains the disordered and ordered carbon phases, as well as the particles of metal-catalyst. The disordered carbon phase is the particles of amorphous carbon, and also so-called of nanoonions. The ordered carbon phase includes single- or

multi-walled CNT and particles of nanographite. Each of the listed phases is characterized by their mechanism of conductivity and, as a result, it has the different temperature dependence of conductivity. We proposed the model of the serial connection of elements with the different conductivity type for describing the transport properties of such complex systems in Ref. [4]. Within the framework of this model the electrical resistance and thermoelectric power of the amorphous carbon were successfully described. Let try to use this model for describing the electrical resistance of the indicated NCM. Here we consider the mechanisms of the conductivity for each phase constituent. It is known; that disordered carbon has the hopping behavior of conductivity with the variable length of jump. For the 3D case the temperature dependence of resistance within the hopping model is described by the equation

$$\rho_{carb} = \rho_0 \exp \left[\left(\frac{T_0}{T} \right)^{\frac{1}{4}} \right], \quad (1)$$

where T_0 and ρ_0 are the coefficients, which values can vary within the wide range depending on the degree of the ordering of amorphous carbon. Single-walled CNT or CNT with a small quantity of walls are the strongly interacting 1D system, which electronic properties, in particular, electrical conductivity are described by the Luttinger liquid theory with the power temperature dependence of resistance:

$$\rho_{NT} \sim T^\alpha. \quad (2)$$

For the ordered carbon phase, i.e., for nanographite and multi-walled CNT, we consider the mechanism of conductivity similar to that existing in the highly oriented pyrolytic graphite

$$\rho_{GR} = e(n\mu_n + p\mu_p). \quad (3)$$

So the character of the temperature dependence of resistance is determined by the character of the temperature dependences of the concentrations of electrons (n), holes (p) and their mobilities (μ_n and μ_p) respectively.

Here we ignore neglected by the conductivity of the metal-catalyst particles. The relative content of the metal nanoparticles in NCM, obtained by different methods, does not exceed 30%. As it was shown earlier for different systems, for example, for the dispersed graphite-metal and thermoexfoliated graphite-metal [5] such content of metal particles does not influence neither the value of electrical resistance nor the character of its temperature dependence.

Thus, the total resistance of NCM is represented as the sum of the series-connected effective resistances, which corresponds to different phases in NCM:

$$\rho = c_{carb} \cdot \rho_{carb} + c_{NT} \cdot \rho_{NT} + c_{GR} \cdot \rho_{GR}. \quad (4)$$

3. Results and Discussion

Let estimate the resistance of NCM of different structural-phase composition within the framework of the proposed model.

For the analysis of NCM electrical resistance the NCM samples obtained by the arc-discharge method were taken. A part of the samples was subjected to thermochemical treatment in order to change its structure and phase composition. The X-ray diffraction analysis and TEM were used to characterize the structure and morphology NCM [3]. The structure and phase composition of each sample are described in Table 1. Evidently, the ratio of ordered (CNT) to disordered phase contents increases from sample I to sample V. Besides the particles of nanographite were found in two last samples.

TABLE 1

Samples #	X-Ray Data	Electron microscopy date
I	No 002-graphite reflexes	Very big particles of amorphous carbon about 20 μm in size, consisted of small particles up to 100 nm in size. Individual CNT of irregular shape
II	No 002-graphite reflexes	Grid of individual tube-like formations in amorphous carbon matrix.
III	No 002-graphite reflexes	Grid of very thin filament-like formations ($d=3$ nm), which are ordered in a certain way, in amorphous carbon matrix
IV	$d_{002} = 3.36\text{\AA}$	Continuous grid of very thin filament-like formations ($d=6$ nm) covered by the particles of the ordered dendrite structure
V	$d_{002} = 3.35\text{\AA}$	Chaotically distributed scroll-like formations with diameter from 60 to 300 nm.

Experimental dependences of resistivity $\rho(T)$ obtained by the procedure [5], are presented in Fig. 1. As can be seen from Fig. 1, the value of resistivity and the character of its temperature dependence essentially differ for different samples. Sample I is the ensemble of the disordered carbon particles, sample II consists of the particles of disordered carbon with an insignificant amount of CNT (see Table 1). It was stated earlier the conductivity of such materials is described by the hopping model with the variable length of jump (Eq. (1)), that is confirmed experimentally (Fig. 2). Sample III consists of the particles of disordered carbon up to 60 nm in size and CNT's ropes ~ 2.4 nm in diameter, i.e., this sample is non uniform, and its conductivity can be described within the proposed model taking into account the first and the terms (Eq. (4)).

In our calculations we used the values of T_0 and ρ_0 the same as those determined from the experimental dependence for sample II, and α value was selected typical for the single-walled CNT ($\alpha \sim 0.44$). Sample IV contains the particles of disordered carbon and CNT and, besides, the particles of the ordered

carbon phase (nanographite). Therefore, for this sample, as for sample V it is necessary to take into account the term in Eq. (4). Since sample V contains only ordered carbon phase and separate CNT assemblies, so term, which corresponds to the conductivity of disordered carbon, should be neglected. To calculate the resistance of the ordered carbon phase we used the values of concentrations and mobilities of electron and holes the same as in Ref. [6]. The results of the performed carried out calculations for 77 and 293 K, the parameters, used for the calculations, and also the values of C_{carb} , C_{NT} and C_{GR} , wich provide the best correlation of the experimental and calculated are represented in Table 2.

Thus, the proposed model of the serial connection of the effective resistances, which correspond to the particles with the different types of conductivity satisfactorily describes the experimental results.

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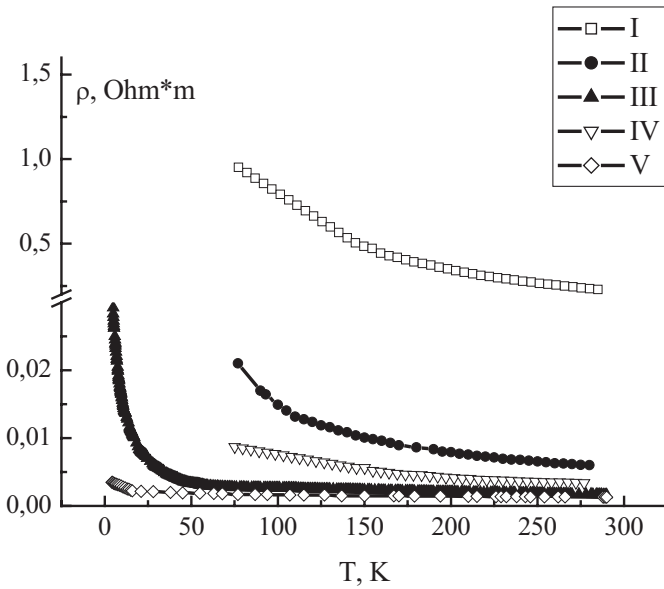


Figure 1. Temperature dependence of electrical resistivity for different NCM samples (Roman numeral on the Figure corresponds to the number of sample in Table 1).

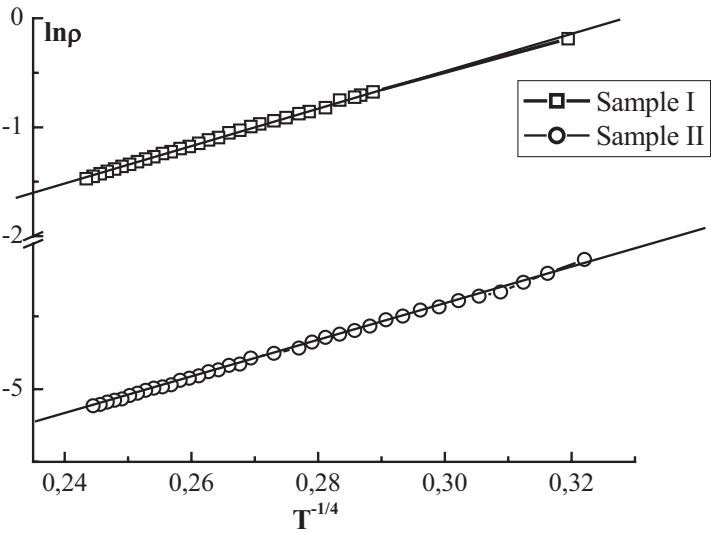


Figure 2. Experimental dependence $\rho(T)$ in coordinates $\ln \rho - f(T^{-1/4})$ for sample I and sample II.

TABLE 2

Sam ples #	Formula for calculation	Coefficient s	ρ_{77} Ohm·m experiment	ρ_{293} Ohm·m experiment
			calculation	calculation
I	$\rho = \rho_{carb}$ $T_0 = 8 \cdot 10^4 K,$ $\rho_0 = 3.7 \cdot 10^{-3} Ohm \cdot m$	$C_{carb} = 1$	1	0.23
			1.1	0.20
II	$\rho = \rho_{carb}$ $T_0 = 2 \cdot 10^4 K,$ $\rho_0 = 1.8 \cdot 10^{-4} Ohm \cdot m$	$C_{carb} = 1$	0.2	$6.0 \cdot 10^{-3}$
			0.24	$8.0 \cdot 10^{-3}$
III	$\rho = c_{carb} \cdot \rho_{carb} + c_{NT} \cdot \rho_{NT}$	$C_{carb} = 0.95$ $C_{NT} = 0.05$	$1.0 \cdot 10^{-3}$	$4.5 \cdot 10^{-4}$
			$1.9 \cdot 10^{-3}$	$7.3 \cdot 10^{-4}$
IV	$\rho = c_{carb} \cdot \rho_{carb} + c_{NT} \cdot \rho_{NT} + c_{GR} \cdot \rho_{GI}$	$C_{carb} = 0.5$ $C_{NT} = 0.2$ $C_{GR} = 0.3$	$8.7 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$
			$7.0 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$
V	$\rho = c_{NT} \cdot \rho_{NT} + c_{GR} \cdot \rho_{GR}$	$C_{NT} = 0.2$ $C_{GR} = 0.8$	$1.6 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
			$3.0 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$

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FREE RADICAL HALOGENATION OF CARBON NANOMATERIALS AT LOW TEMPERATURES

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Abstract. It has been revealed that carbonic nanomaterials (fullerene, single- and multiwall nanotubes, nanofibers) display high activity at low temperatures (77K) in reactions of chain halogenation (F_2 , Cl_2) with kinetic chain length up to $10^4 - 10^5$. The ESR spectra of active free- radical intermediates were recorded. The presence of vibration bands of C–Cl bonds in products has been indicated by IR method.

Keywords: carbonic nanomaterials, halogenation, low temperatures, ESR spectroscopy

1. Introduction

One of the leading tendencies in chemistry of nanomaterials is their modification for obtaining new properties. Halogenation as one of efficient methods of modification is of great interest because both chlorine- and fluoro- derivatives should serve molecular intermediates for further modification. Chemical transformations of the attached functional groups give the base for the creation of principally new spatial structures based on carbonic nanomaterials.

Previously we have investigated solid phase halogenation reactions forming free radicals at low temperatures (30–200K) which proceed under direct interaction of molecular chlorine and fluorine with polymeric materials. It has been shown that halogenation reactions are chain ones and they efficiently produced free radicals. The initiation stages were considered in the framework of model of multi-center reactions in polymolecular complex with participation of molecular chlorine and fluorine [1, 2]. These methodical approaches developed for investigation of solid phase halogenation reactions of polymeric systems, have been used in present work to reveal the extreme reactivity abilities of nanomaterials at low temperatures and to investigate by ESR and IR spectroscopy methods as well as by methods of elemental and gravimetric analysis of processes of low-temperature halogntation and fluorination of fullerenes C_{60} , single- and multi-wall nanotubes, nanofibres etc. and for their functionalization to obtain appropriate precursors.

2. Experimental

Fullerene demonstrate inherent paramagnetizm in ESR spectra as narrow singlet line with width $\Delta H = 0.2$ mT and $g = 2.002$ (Fig. 1, spectrum 1), sometimes

additional singlet at $g=1.998$ appears (spectrum 2). These paramagnetic centers (PMC) can be caused by structural defects or by remains of synthesis or refining [3]. Their concentrations for different fullerenes are $3 \times 10^{17} - 4 \times 10^{15}$ spin/g. During the contact of C_{60} with molecular fluorine at 77K new signal with $\Delta H=1,7$ mT and $g=2,0023$ arises, another narrow slight signal can be seen in its central part (spectrum 3). The new signal in the contrast to inherent PMC signal is not saturate even at microwave power as high as 5,0 mW and it can be reliably distinguished (spectrum 4). The PMC density grows for the account of fluorination up to 3×10^{19} spin/g. The PMC thus obtained possess high stability and both their number and spectrum shape do not change under heating to 373K.

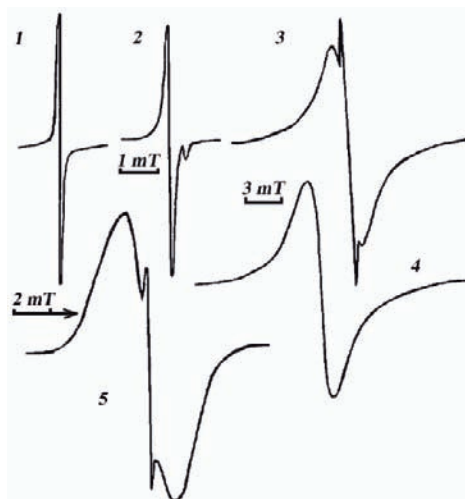


Figure 1. The ESR spectra of fullerene C_{60} (1, 2), and that fluorinated (3, 4) and chlorinated (5) at 77K.

Unlike the fluorine interacting with practically any type of chemical bonds the molecular chlorine at low temperature selectively interacts with double bonds of olefin series. To overcome the high activation energy for common chlorination the UV light has been applied to dissociate molecular chlorine to atoms.

Necessary condition for chlorine atoms chemical reaction with solid nanomaterials was the samples preliminary annealing in liquid chlorine during several hours, then they were subjected to UV radiation ($\lambda \geq 360$ nm) at 77 or 200K. In the ESR spectra arisen at the free radical driven fullerene C_{60} chlorination presented the singlet lines with different width ($\Delta H=1.5-2,7$ mT, $g=2.000$), the last is possibly connected with variations in the conditions of preliminary processing and in the duration of their exposition to UV radiation (Fig. 1, spectrum 5). The singlet lines of fluorinated fullerene can be assigned as PMC on conjugated molecular systems that represent fullerene accepted several chlorine atoms. The fact of chlorine presence in conjugated system is evidenced as well by the weakening of saturation effects in ESR signal of chlorinated sample in comparison

with the signal belonged to pure C_{60} . The last is the consequence of both the strong spin-lattice coupling in chlorine containing PMC and the growth of the spin-lattice relaxation rate.

In dependence of chlorination conditions the PMC densities were 7×10^{16} – 1.3×10^{18} spin/g (PMC background density was 4×10^{15} spin/g and $\Delta H = 0.2$ mT, $g = 2.002$). Unlike PMC in fluorinated samples the chlorinated ones are unstable and their density drops 10 – 15 times under heating from 250 to 400 K.

Gravimetric and elemental analysis lead to the following brutto-formula for the products of fullerene chlorination $C_{60}Cl_n$ ($n = 2 \div 8$). The broad bands in IR spectra (Fig. 2) close to characteristic vibrations for C–Cl bonds (frequencies 885, 850 and 808 cm^{-1}) evidenced the presence of the mixture different isomers in the sample [4].

The hydrocarbon chlorination reactions usually display the radical-chained character of their mechanisms. Such a mechanism can be suggested as well for low temperature photoinduced chlorination of carbon nanomaterials. The kinetic chain length in this process is as high 3×10^4 – 10^6 (for chlorides of $C_{60}Cl_2$ and $C_{60}Cl_8$ compounds correspondingly).

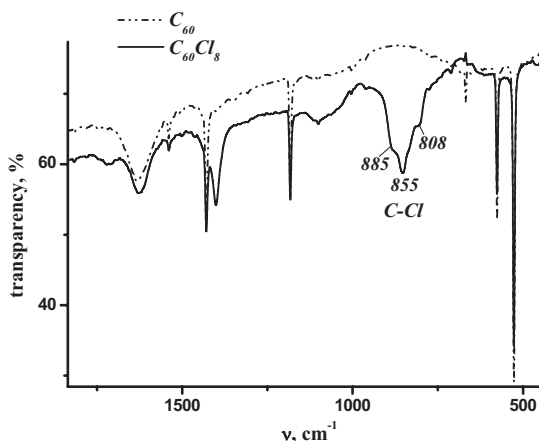


Figure 2. IR spectra of chlorinated fullerene.

Elemental analysis of chlorinated samples of carbonic nanofibers and multiple wall nanotubes revealed that the abundance of chlorine in compounds obtained is 5,8 and 1,3 mass. %, respectively.

3. Conclusion

Thus, for the first time it is shown that carbonic nanomaterials (fullerene, single- and multiwall nanotubes, nanofibers) demonstrate high activity at cryogenic conditions (77 K) in reactions of chain halogenation (F_2 , Cl_2) with kinetic chain length up to 10^4 – 10^5 . The ESR spectra of active free-radical intermediates were recorded. The presence of vibration bands of C–Cl bonds in products has been indicated by IR method. For the first time chain fluorination of carbonic nanofibers, mono- and multiwall nanotubes has been performed at low temperatures.

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HYDROGEN CONCENTRATION DEPENDENCE ON THERMAL AND ELECTRICAL CONDUCTIVITIES OF METAL-HYDRIDE COMPOSITE MATERIALS

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Abstract. Thermal conductivities of uranium-zirconium hydrides (45 wt%U-ZrH_x : x=1.60 and 1.90) have been calculated at temperature up to 773 K by taking into account the thermal diffusivity, measured using a laser-flash method, the specific heat and the density. The thermal conductivity increased with increasing the content of hydrogen retained in ZrH_x. Moreover, the electronic and phonon heat conductions have been estimated from Wiedemann-Franz rule and electrical conductivity, obtained using a four-contact DC method. The increment of the conductivity is attributed to the phonon as well as electron scatterings due to hydrogen vacancy in the hydrides. The contribution by the phonons was greater than that by the electrons at temperatures below 500 K, while both electrons and phonons play an important role in the thermal conductivity above 500 K.

Keywords: Metal-hydride composite materials; Thermal diffusivity; Thermal conductivity; Electrical Resistivity

1. Introduction

A transmutation method of actinide radioactive wastes with irradiation hydride targets, which are loaded with the formation of pellets in the core region of fast breeder reactors containing mixed oxide fuels, has been proposed recently [1]. The hydrides are composed in the target materials and play a role as a neutron moderator to gain high flux of thermal neutron. During the irradiation, the gradient of temperature takes place between the parts of center and edge in the targets and the distribution of hydrogen concentration changes with hydrogen diffusion [2]. For designing of the hydride targets, it is extremely important to investigate the changes on the mechanical, thermal and electrical properties for various hydrogen. So far, the hydrogenation, mechanical and thermal properties of metal-hydride composite materials such as uranium-thorium-zirconium hydride or uranium-zirconium hydride have been investigated [1-6]. In the present study, thermal diffusivity and electrical resistivity of 45 wt%U-ZrH_x were measured, and heat conductions due to free electrons and phonons were discussed.

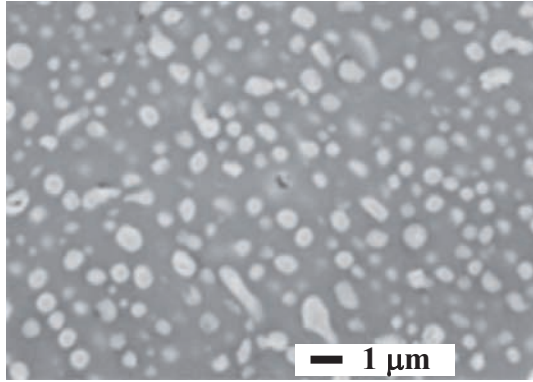


Figure 1. SEM image of 45 wt%U-ZrH_{1.60}, composed with U (white part) and ZrH_{1.60} (dark part) phases.

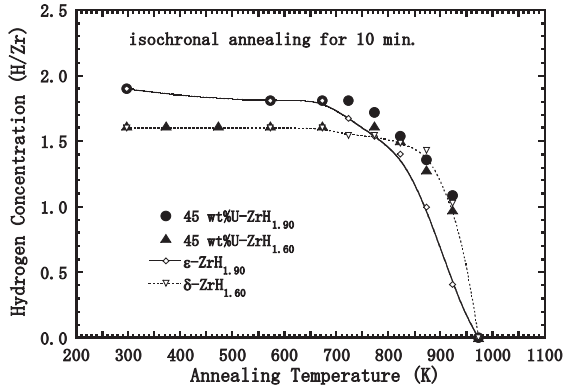


Figure 2. Changes of hydrogen concentrations in U-ZrH_{1.60}, U-ZrH_{1.90}, ZrH_{1.60} and ZrH_{1.90} after isochronal annealing at several temperatures for 10 min.

2. Experimental

45 wt%U-ZrH_{1.60} and U-ZrH_{1.90} composite materials were fabricated by a hydrogenation of U-Zr alloy with Sieverts apparatus [3]. It was observed from a scanning electron microscope (SEM) that the specimens consisted of two phases such as U and ZrH_x. U phase of about 1.0 μ m diameter is dispersed in the bulk of ZrH_x phase, as shown in Fig. 1. The value of H/Zr ratio was determined by the mass changes before and after the hydrogenation. Moreover, the hydrogen composition as well as the structure were confirmed by X-ray diffraction (XRD) measurements that ZrH_{1.60} and ZrH_{1.90} had face-centered cubic (δ -phase) and face-centered tetragonal (ϵ -phase) structures, respectively.

Figure 2 shows hydrogen release from $\text{U-ZrH}_{1.60}$, $\text{U-ZrH}_{1.90}$, $\text{ZrH}_{1.60}$ and $\text{ZrH}_{1.90}$ by an isochronal annealing for 10 min at several temperatures of 298~973 K. The interesting results are shown in Fig. 2 that the decomposition temperature of 823 K for $\text{U-ZrH}_{1.60}$ is the same with that for $\text{ZrH}_{1.60}$, while that of 773 K for $\text{U-ZrH}_{1.90}$ is higher than that for $\text{ZrH}_{1.90}$. To avoid the reduce of the hydrogen concentration by hydrogen molecular re-emission, special specimen containers, made of sapphire, were used for the thermal diffusivity measurement [4]. The heating temperatures were successful in elevating up to 900 and 840 K for $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$, respectively, during a thermal diffusivity measurement with a laser flash method. Moreover, the electrical resistivity measurement was carried out from room temperature to 773 K using a four-contact DC method, in order to estimate the each fraction of the heat conductions due to free electrons and phonons.

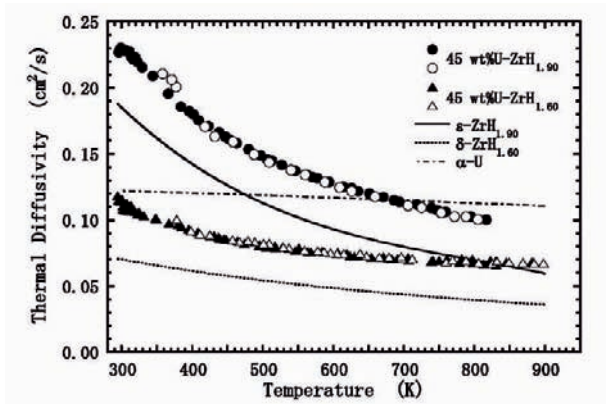


Figure 3. Thermal diffusivities of $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$, as compared with those of $\text{ZrH}_{1.60}$, $\text{ZrH}_{1.90}$ and U.

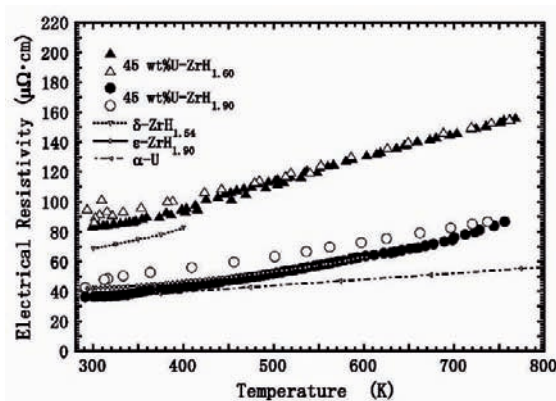


Figure 4. Electrical resistivities of $\text{U-ZrH}_{1.6}$ and $\text{U-ZrH}_{1.90}$, as compared with those of $\text{ZrH}_{1.54}$, $\text{ZrH}_{1.90}$ and U.

Results and discussion

Figure 3 shows thermal diffusivities of $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$, measured with increasing (●, ▲) and decreasing (○, △) the heating temperature. The coincidence between the values on heating and cooling represents no hydrogen release from the specimen. The thermal diffusivity of U-ZrH_x increased with increasing hydrogen concentration and with decreasing the temperature. The temperature dependence of thermal diffusivity for U-ZrH_x is similar to that for ZrH_x [7], though the absolute values are different. Because the thermal diffusivity of U is nearly constant in the temperature range up to 900 K [8], as shown in Fig. 3. The present experimental values are about 1.5 times as much as those of 10 wt%U-ZrH_x [6] because the amount of U doped is more.

In order to clarify electronic heat conduction for U-ZrH_x , the electrical resistivity was measured with heating up to 773 K and cooling down to room temperature. Figure 4 shows electrical resistivities of $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$ on heating (●, ▲) and cooling (○, △). In the $\text{U-ZrH}_{1.90}$ specimen case, the distortion between the values on heating and those on cooling shows the reduce of hydrogen concentration, caused by hydrogen release from $\text{ZrH}_{1.90}$. The electrical resistivities of U-ZrH_x increased as the temperature increased and the hydrogen concentration decreased. The hydrogen concentration dependence on the resistivity of U-ZrH_x dominates those of ZrH_x [7, 9] rather than that of U [10], and is caused by electron scattering due to hydrogen vacancy in the hydrides. The resistivity behavior at higher temperature is caused by scattering of electrons due to acoustic phonons as well as optical phonons [7, 9].

Figures 5 (a) and (b) show the thermal conductivities (λ) of $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$, respectively, at the temperatures up to 773 K which were calculated from the relation of $\lambda = \alpha C_p d$, where α , C_p and d represented the thermal diffusivity, the specific heat and the density, respectively. It has been already demonstrated that the values of C_p and d can be expressed as the simple functions of temperature and composition [11]. The high thermal conductivity at irradiation temperature of 700 K induces to the safety at high linear power in reactors.

The thermal conductivities of $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$ by electronic conduction (λ_e), plotted as (▲, ●) in Figs. 5 (a) and (b), were estimated from the relations of $\lambda_e = L_e \sigma T$, according to the Wiedemann-Franz rule. σ is the electrical conductivity ($\sigma = 1/\rho$), where ρ is the electrical resistivity, L_e is the Lorenz number for the electronic conduction, assumed as $L_e = (\pi^2/3)(k_B/e)^2 \doteq 2.45 \times 10^{-8} [\text{W}\Omega/\text{K}^2]$, where k_B and e are the Boltzmann constant and elementary electric charge.

Finally, the thermal conductivities of $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$ by phonon conduction (λ_p), plotted as (△, ○) in Figs. 5 (a) and (b), were determined by subtracting λ_e from λ . At lower temperatures, the contribution by the phonons was greater than that by the electrons, while both electrons and phonons play an important role in the thermal conductivity above 500 K.

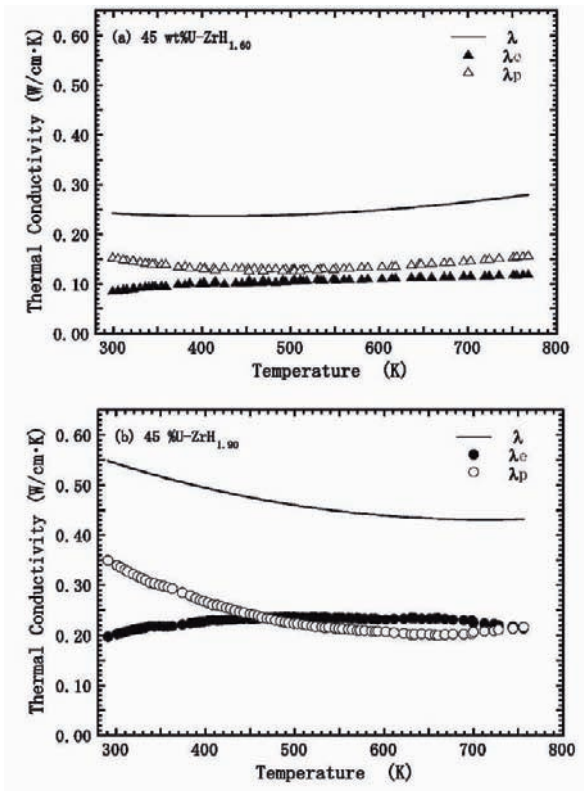


Figure 5. Thermal conductivities λ of (a) $\text{U-ZrH}_{1.60}$ and (b) $\text{U-ZrH}_{1.90}$. λ_e and λ_p represent the thermal conductivities due to free electrons and phonons, respectively.

3. Conclusion

The thermal diffusivities of the metal-hydride composite materials such as $\text{U-ZrH}_{1.60}$ and $\text{U-ZrH}_{1.90}$ were measured and their thermal conductivities were estimated by taking into account the density and the specific heat. The thermal conductivity greatly depended on one of hydrides and increased with increasing the hydrogen concentration. The heat conduction due to electrons and phonons were distinguished using Wiedemann-Franz rule and the electrical conductivity. The phonon-phonon scattering is dominant for the thermal conduction at room temperature, while the electronic and phonon heat conduction contribute at almost same fractions for the thermal conductivities of U-ZrH_x at high temperatures above 500 K.

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IRRADIATION EFFECT OF GAMMA-RAY ON THE PROTON-CONDUCTING POLYMER

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Abstract. Gamma-ray radiation induced change in the electrical conductivity of the proton-conducting polymer, perfluorosulfonic acid membrane, was investigated. The electrical conductivity increased with increasing the absorption dose in linear form at 300 K and hereafter gradually increased up to be higher by about three orders of magnitude. The conductivity greatly depended on the humidity in vacuum or air. Moreover it was observed by optical absorption measurement that radiation induced defects such as fluorocarbon and peroxy radicals and C=O groups increased with increasing the dose. Therefore, the increase of the conductivity is attributed to conduction due to protons produced by absorption of H₂O with the radiation induced defects.

1. Introduction

Perfluorosulfonic acid membrane, such as Nafion®, Aciplex® and Flemion® are used as electrolyte membrane for fuel cell because of having a high proton conductivity around 373 K [1]. So far, it has been proposed that the polymer is modified easily by the cross-linkage and chemical bond breaking due to X-ray irradiation [2]. It is expected that these phenomenon introduce to a change in the proton conduction of the proton-conducting polymer, and the electrolyte is applied at near room temperature. In the present study, Aciplex® membrane was irradiated by gamma-ray, and the electrical and optical properties were investigated.

2. Experimental

The sample used for the experiments is Aciplex-SF-1004® (10x10x0.117 mm³). The sample was irradiated at room temperature and atmospheric pressure with 1.17 and 1.33 MeV gamma-ray from a cobalt-60 source in the Takasaki Research Establishment of Japan Atomic Energy Research Institute (JAERI). The absorption doses of the sample by gamma-ray were from 1 to 173 kGy.

The electrical conductivity was obtained using the applied voltage and the measured current and dimension of the sample. The electrode was Al plate. For dose dependence, the conductivity was measured at 300 K and at humidity of 40 % in air. For temperature dependence, the conductivity was measured in the temperature range from 300 to 393K in vacuum under pressure of 6×10^{-5} Pa.

In order to understand the change in the conductivity by irradiation, optical absorption measurement were carried out in the wavelength of 190–500 nm using a SHIMADZU UV-2200A.

3. Results and discussion

3.1. CONDUCTIVITY MEASUREMENT

Figure 1 shows electrical conductivity measured at 300 K in air, after gamma-ray irradiation at the several doses up to around 170 kGy. The line described in Fig. 1 shows linear function expressed as $\sigma = 4 \times 10^{-8} D + 10^{-8}$. Here, σ is the conductivity and D is absorption dose of the samples. So the conductivity increased with increasing the absorption dose in linear form. The conductivity at 170 kGy was high by about three orders of magnitude than that of unirradiated one.

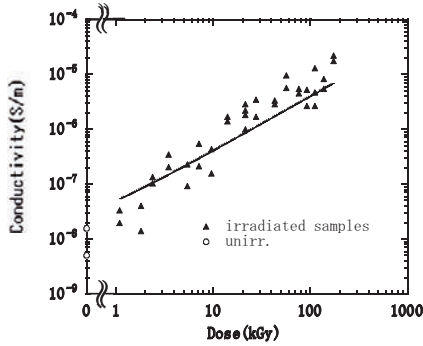


Figure 1. Electrical conductivity at 300 K as a function of absorption dose by gamma-ray irradiation.

Figure 2 shows Arrhenius plots of conductivities for samples unirradiated and irradiated by gamma-ray at 14 kGy in temperature range of 300-393 K in vacuum. The Arrhenius plot for unirradiated sample has one slope. The activation energy, calculated from the slope, is about 0.84 eV and is associated with proton behavior in sulfonate group. On the other hand, The Arrhenius plots for irradiated samples have two slopes in the temperature ranges 300 to 343 and 343 to 393 K, respectively. The activation energies of the conductivities at lower and higher temperatures were determined to be about 0.16 eV and 0.84 eV. Their values indicate two kinds of conduction mechanisms, new conduction produced by irradiation and the existing protonic conduction. And there is the difference

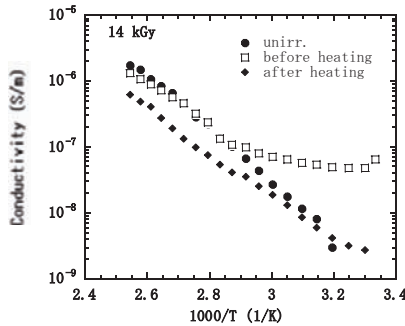


Figure 2. Temperature dependance of electrical conductivity for the sample irradiated at 14 kGy.

between the Arrhenius plots before and after heating in vacuum. After heating the conductivity at lower temperature is similar to that for unirradiated sample. Result indicates that the new conduction mechanism produced by irradiation disappear.

Figure 3 shows changes of electrical conductivity at 300 K against absorption dose measured in some environment such as air or vacuum under a pressure of 6×10^{-5} Pa. Dose dependence of electrical conductivity is same tendency between air and vacuum before heating but the absolute values in vacuum are lower by about two orders of magnitude than those in air. The conductivity decreased by heating to 393 K in vacuum as shown in Fig. 2. When the sample heated to 393 K in vacuum was exposed in air for 20 days, the conductivity of the sample increased again and is same tendency of the result measured in air before heating. These results are caused by changes of humidity in the environment and indicate that the new conduction mechanism disappear after heating. Namely, the protons produced by absorption of water greatly contribute to the new conduction mechanism.

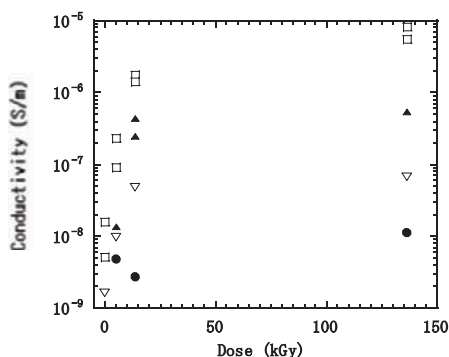


Figure 3. Changes of electrical conductivity at 300 K as a function of absorption dose, measured in air before(□) and after(▲) heating and in vacuum before(▽) and after(●) heating.

4. UV-Vis optical absorption

The optical absorption of the unirradiated and irradiated samples was measured. The spectrum of unirradiated sample has two peaks at 200 and 275 nm. The intensity absorption of ultraviolet region increased with increasing the dose and new absorption band was observed at 215 nm after gamma-ray irradiation. The optical densities normalized by that of unirradiated sample as shown in Fig. 4. Several absorption peaks at 200, 215 and 275 nm were associated with fluorocarbon and peroxy radicals and C=O groups respectively [3]. The cross-linkage and chemical bond breaking of the polymer chain were caused by gamma-ray irradiation.

Figure 5 shows the dose dependence of normalized optical density at the wavelength of 200, 215 and 275 nm. The intensities of absorption band around 200 and 215 nm increase with increasing absorption dose in linear form, while that around 275 nm is nearly constant. The results may indicate that these radicals and unsaturated bond contribute to the increase of electrical conductivity for the irradiated samples.

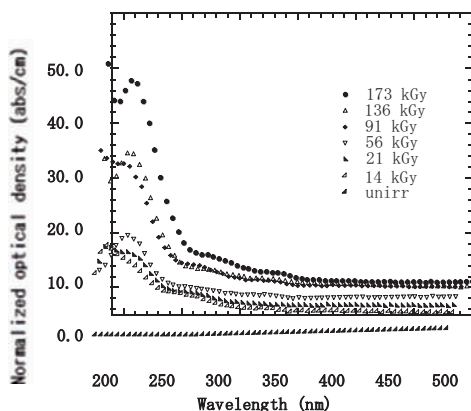


Figure 4. Normalized optical density obtained by subtracting the optical density of unirradiated sample from those of the irradiated ones.

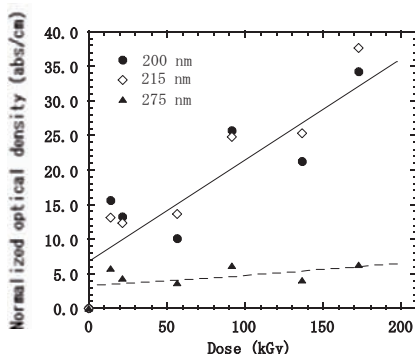


Figure 5. Dose dependence of the normalized optical density at the wavelengths of 200, 215 and 275 nm.

5. Conclusions

The electrical conductivity of the irradiated sample increased in linear form against absorption dose and was higher by three orders of magnitude than that of unirradiated one at room temperature. For temperature dependence on the conductivity, Arrhenius plot for irradiated samples have two slopes, in the temperature ranges 300 to 343 and 343 to 393, respectively. The activation energies at lower and higher temperatures were determined to be 0.16 and 0.84 eV, respectively and show the new protonic conduction with some radicals produced by gamma-ray irradiation and existing proton conduction with sulfonate group. The slope with lower activation energy disappeared by heating to 393 K, and the proton conduction recovers with the exposure in air for enough time.

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ELECTRICAL EXPLOSION TECHNOLOGY FOR NOVEL CARBON NANOMATERIALS PRODUCTION

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Abstract. There were developed two new technologies for manufacturing of novel carbon nanomaterials (fullerenes, nanotubes, carbonic nanoclusters) based on the idea of high-energy plasmochemistry synthesis with the use of the techniques of electrical wire explosion and spark erosion of graphite and metallic materials (nickel, iron, copper) in organic medium. A wide spectrum of fullerene-like materials including the highest ones (C_{70} and higher) was discovered and studied using X-ray diffraction analysis, electron microscopy and mass-spectroscopy. Ferromagnetic properties of carbon nanomaterials were detected and studied. An important role of catalysts in the process of carbon nanomaterial formation was established.

Keywords: carbon nanomaterials, exploding wires, spark erosion, fullerene-like clusters, ferromagnetic nanomaterials

1. Introduction

New spatial forms of carbon – fullerenes, nanotubes, nanowires and nanofibers attract significant interest since the time of their discovery due to their unique physicochemical and mechanical properties [1-3]. There are three basic methods of manufacturing of the carbon nanomaterials (CNM) – laser evaporation, electric arc process, and catalytic pyrolysis of hydrocarbons. However, the multi-stage manufacturing process is a serious disadvantage for all of them. For example, the use of organic solvents (benzol, toluene, etc.) for separation of fullerenes from graphite soot results in delay of the synthesis process and decrease in the final product quantity. Moreover, some environmental problems can arise at this.

Much investigation has been carried out in this field in the recent years. Hence, the problem of development of effective synthesis methods of CNM as well as those of separation and purification remains of actual importance. Therefore, the question of development of new effective one-stage methods for the CNM synthesis is of great interest.

The purpose of this research is to study a possibility to manufacture CNM (fullerenes, nanotubes, amorphous carbon, etc.) using a high-energy plasmachemistry synthesis, namely spark erosion (SE) and exploding wires (EW) techniques. Moreover, of some interest is an effect of the synthesis parameters (energetic flows, time-energy parameters of the electrical impulses, surrounding operating medium, presence of different catalysts, etc.) on the spectrum of CNM, their structural and physical properties.

2. Experimental procedures

EW and SE methods of high-energy plasmachemistry synthesis have been used for CNM manufacturing. Chemically pure (99.99 %) elements were used as the starting materials.

In the SE method, the spark discharge is initiated and maintained between two electrodes or granules of electrical conducting materials [4-6]. In these conditions a plasma channel of about 50 μm in diameter arises in the space between the electrodes. The temperature in the plasma channel increases up to 10^4 K and the pressure can reach several hundreds MPa. As a result, some of electrode material melts and evaporates. After the end of the spark discharge, the pressure declines sharply, and superheated areas of the melt boil up. This causes the emission of the drops and vapor of the material into surrounding operating fluid. Upon the contact with the fluid they quench with a rate as high as 10^9 K/s. Two types of the particles were observed: the first one formed of the molten drops is in the range of 0.5 – 50 μm , and the second one originated by the condensation of vapor is in range of 5 – 50 nm.

CNM manufacture using the EW method is performed by means of advancing of high energy brief electrical impulse through a sample fixed between two electrodes placed into the operating chamber filled with an inert gas or dielectric medium [4,7]. Through appropriate selection of time-energy parameters of the electrical impulses transformation of the sample into the vapor-plasma state can be achieved. The subsequent fast cooling of the plasma channel causes recombination of the ions into atoms. They are associated into clusters or particles by the atoms collision. In case of use of dielectric liquid as the surrounding medium the cooling rate can reach up to $10^{10} - 10^{14}$ K/s. At such rate recombination particles in the range of 1 to 100 nm in diameter are obtained, which was revealed by the TEM investigation. The mean particle size and their structure state are determined by time-energy parameters of the electrical impulse and physicochemical properties of the operation medium. At the specified conditions the fine particles can be obtained in different structural states: crystalline, amorphous-crystalline, quasi-crystalline, and amorphous ones.

X-ray diffraction (XRD) investigations were performed by means of a standard powder diffractometer using Cu K_α radiation. Electron microscopy investigations were conducted using the Hitachi H-800 microscope operated at voltage of 200 kV. The magnetic properties were measured by means of the ballistic method in the magnetic field up to 800 kA/m in the temperature interval of 77 to 673 K.

Mass-spectrometer measurements were performed by the method of the field desorption using a high resolution device (resolution ratio is about 1000, operating

voltage is 7.5 kV, the collector current of main component is about 10^{-12} A) to find fullerenes and carbon clusters (up to 2000 amu) in synthesis products.

3. Results

Produced by the EW technique CNM were subjected to investigation using XRD analysis, electron microscopy, and mass-spectrometer analysis. The typical XRD patterns for the exploded materials in different conditions are shown in Fig. 1 and Fig. 2. It is immediately obvious that there is a presence of additional diffraction peaks at small angle values besides those typical for common graphite. This fact clearly demonstrates the appearance of new structural compositions in the synthesis products. A phase analysis performed shows that these diffraction peaks correspond to those for carbonic spatial materials with the fullerene-like structure of the C_{60} - C_{70} types.

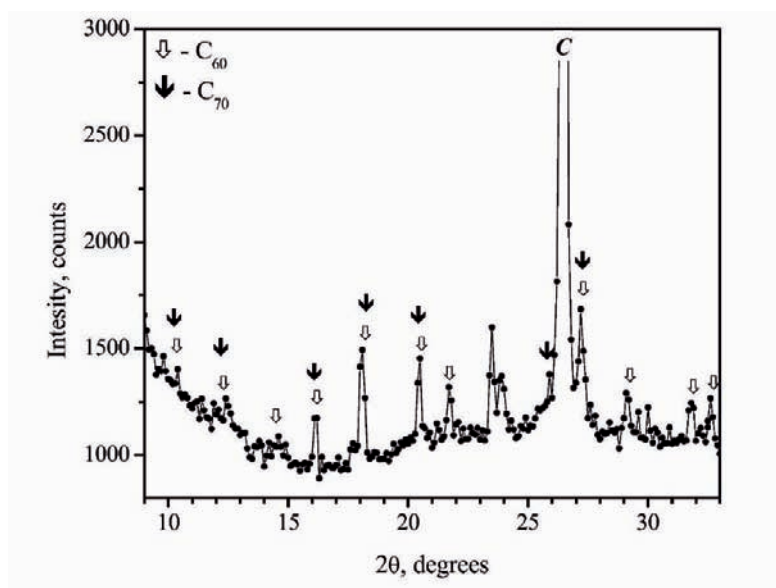


Figure 1. Fragment of the XRD pattern of the graphite explosion products in the toluene at the operational voltage of 20 kV, Cu K_{α} radiation.

Mass-spectrometer studies were performed to testify this assumption. The spectral compositions of CNM produced through explosion of graphite, iron, and nickel wires in toluene are shown in Table 1. The fact of presence of CNM of high masses in case of graphite-free explosive materials is of great interest. In this case there is a set of masses typical for both lower fullerene-like materials and the highest ones in the synthesis product. An electron microscopy investigation of both the liquid and deposit shows a presence of the nano-dispersive carbon particles, agglomerations of nanotubes and separate nanotubes (Fig. 3).

It should be particularly emphasized that there is a fundamental possibility to manufacture diamond-like nanomaterials at this conditions. The XRD study of synthesized CNM testifies that some diffraction peaks correspond to the diamond phases (Fig. 2).

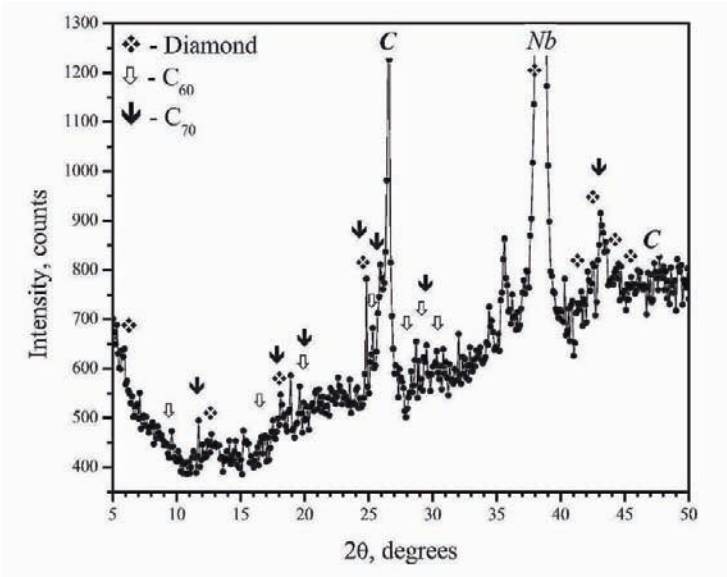


Figure 2. Fragment of the XRD pattern of the graphite explosion products in ethanol at the operational voltage of 45 kV, Cu K α radiation, Nb-substrate.

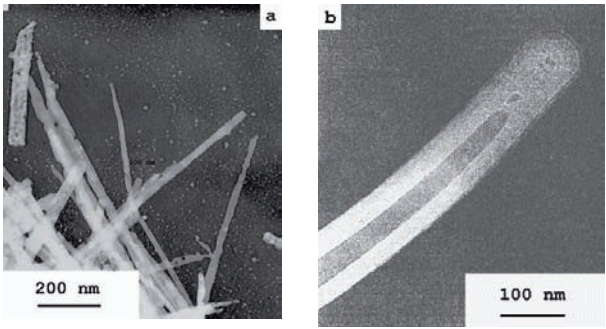


Figure 3. Electron microscopy images of the graphite (a) and nickel (b) explosion products in the toluene: a) agglomeration of nanotubes, b) separated multi-walled nanotube.

It is worthy of note that EW products have very strong ferromagnetic properties in a number of cases. Dependence of magnetization versus temperature corresponding to the separated magnetic fraction of EW products is represented in Fig. 4. The magnetization curve is typical to those of ferromagnetics.

It was very important to explore the possibility to manufacture new forms of CNM using the SE method. It has a very high productivity and can be used for commercial purposes. The spectral compositions of the synthesis products obtained by the SE method using the graphite electrodes and different surrounding mediums are represented in Table 2. It is well seen that a set of fullerene-like materials can be produced by the SE method, too.

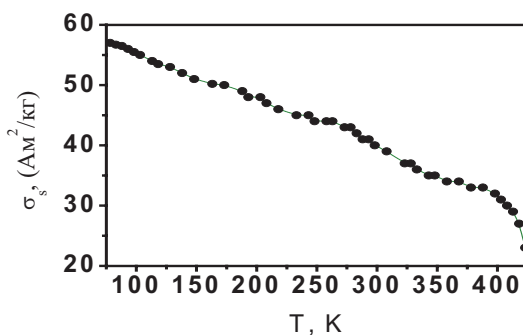


Figure 4. The temperature dependence of specific magnetization of the graphite explosion products.

TABLE 1. Spectral composition of the fullerene-like clusters produced by EW method in the case of explosion of different materials in the toluene at the next technological parameters – U=4.5 kV, E= 20 kJ, τ=1 ms

№	Explosive material	Spectral composition, amu
1	C	463, 493, 542, 576, 658, 740, 768, 852, 875, 919
2	Fe	304, 316, 328, 344, 356, 368, 721, 864
3	Ni	532, 560, 589, 623, 860

TABLE 2. Spectral composition of the fullerene-like clusters produced by SE method in the case of using graphite in different surrounding mediums at the next technological parameters – U=180 V, C= 10 μF, τ=10 ms

№	Operational medium	Spectral composition, amu
1	ethanol	363, 376, 390, 404, 418, 432
2	benzine	447, 474, 477, 502, 532, 558
3	toluene	477, 506, 533, 561, 604, 828, 858, 881, 885

4. Discussion

Now, the use of both the EW and SE methods provides a possibility to manufacture novel CNM – fullerenes, nanotubes, etc. In this case we can reach the conclusion, that CNM are produced under very non-equilibrium conditions, namely under conditions of the high-energy plasmachemistry synthesis in organic mediums. At this juncture intensive flows and extreme densities of matters occur. It results in production of CNM due to self-organization and directional catalytic transformations.

The fact of production of the fullerenes without the use of graphite as material for the synthesis is of significant scientific interest and importance (Table 1). It can be explained as a result of destruction of surrounding organic (toluene, benzol, benzene, alcohol, etc.) medium with following directional self-organization of destruction products and CNM formation under condition of the high-energy plasmachemistry synthesis (temperature and pressure values amount to 10^4 K and 300-500 MPa, accordingly). At the specified conditions there is the effective possibility to control the spectral composition of the synthesis products through variation of synthesis energetic parameters and surrounding medium. It should be particularly emphasized that there is a fundamental possibility to manufacture diamond-like nanomaterials at these conditions. The XRD study of synthesized CNM (Fig. 2) testifies that some diffraction peaks correspond to the diamond phases. But this assumption should be examined by the use of a set of investigation techniques, since the XRD patterns for graphite and diamond are very similar to each other in a number of cases.

One should note the significant role of the catalysts at the CNM formation process. Thus, the use of nano-sized nickel particles as catalyst in case of explosion of graphite in toluene results in formation of high fullerene-like clusters with masses of 882 and 884 amu, which are close to C_{70} fullerene. While the wide cluster spectrum is formed in case of graphite explosion in pure toluene. The catalyst influence upon magnetic properties of the synthesis products should be noted, too. Thus, adding of 0.4 at. % Fe only results in ferromagnetic state of the deposit in case of graphite explosion in toluene (Fig. 4). Contribution of such amount of iron into whole magnetization is less than 1 %. So we have a ferromagnetic state of carbon, possibly containing complexes of iron.

A ferromagnetic state of the synthesis products was observed also in case of use of nano-dispersive copper as the catalyst. It should be noted that the CNM can have magnetic properties in case of catalyst-free synthesis, but the magnetization value is within the limits of $1\text{--}5\text{ A}\cdot\text{m}^2/\text{kg}$. The magnetic properties of C_{60} polymers with relatively low values of magnetization were studied in [8], too.

It may be safely suggested that origin of the ferromagnetic state in the synthesis products is a result of change in their electronic structure at the high-energy plasmachemistry synthesis. It results in the appearance of carbonic clusters with unpaired electron spins and formation of ferromagnetic domains with equally oriented spins.

5. Conclusions

1. There were developed two new technologies for manufacturing of novel carbon nanomaterials (fullerenes, nanotubes, carbonic nanoclusters) based on the idea of high-energy plasmochemistry synthesis with the use of the methods of electrical wire explosion and spark erosion of graphite and metallic materials (nickel, iron, copper) in organic medium.

2. The above-mentioned methods allow to produce a wide spectrum of fullerene-like materials including the highest ones – C_{70} and higher (up to 1338 amu in our case). The fact of production of the fullerenes without the use of graphite as a material for the synthesis is of great scientific interest and importance. There exists an effective possibility to control the spectral composition of the plasmochemical synthesis products through variation of the energy parameters of the synthesis and surrounding medium.

3. An important role of the catalysts (Ni, Cu, Fe) for the spectral composition, structural state and physical properties of the carbon nanomaterials produced with the electrical wire explosion and spark erosion methods was established.

4. It was discovered that the plasmochemical synthesis products have ferromagnetic properties. The magnetization value of the synthesized carbon nanomaterials amounts the value close to the one of typical ferromagnetics.

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PROMISING CATALYSTS FOR H₂ - O₂ FUEL CELLS (REVIEW)

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Abstract. The aim of the present paper is to give the review of the recent investigations in the field of non-noble metal catalysts (group 1) and in the field of catalysts containing reduced amount of a noble metal due to the improvements in the technology of their preparation (group 2). Some novel electrocatalysts of oxygen reduction and hydrogen oxidation from both these groups are considered in this paper.

Keywords: electrocatalysts, oxygen reduction, hydrogen oxidation, fuel cells.

1. Introduction

The electrochemical storage of energy and its conversion are of great interest from the point of view of many practical applications. The market for portable fuel cells and batteries to electronic devices has recently strong tendency to expansion. Due to the requirements of environmental protection, a lot of research work is also devoted to the application of fuel cells and promising batteries in electrical vehicles. From the economical point of view and due to the requirements of the ecology there is a big demand for relatively low cost and environmentally friendly electrode materials and catalysts to be used for fuel cells and batteries. The decisive factors that must be taken into account when estimating the possibility of wide application of fuel cells are the cost and the effectiveness of the catalyst. The most important parts of fuel cells are electrocatalysts. They determine a cost and system capability of fuel cells. Mainly the noble metals (Pd, Pt) are used recently as anode and cathode catalysts in fuel cells. The most effective catalytic materials appear to be the materials prepared in the form of a thin layer of active catalyst precipitated at the surface of carbon, ceramic or other porous materials with a highly developed surface.

As fuel for fuel cells are used commonly hydrogen, methane, methanol, metal hydrides and other substances. Hydrogen has the highest weight specific energy (32,702 W·h/kg). The main types of hydrogen fuel cells are following:

1. Alkaline (AFC): These are used by NASA on the manned space missions, and operate well at about 80 °C. They use alkaline electrolyte, potassium hydroxide, and can generate electricity with the efficiency up to 70 %.

2. Proton Exchange Membrane (PEMFC): These cells use a perfluorinated ionomer polymer membrane which passes protons from the anode and cathode. They operate at about 80 °C. These are being developed for use in transport applications and for portable and small fuel cells.

3. Phosphoric Acid (PAFC): This is the most commonly used type of a fuel cell for stationary commercial sites like hospitals, hotels and office buildings. The cell operates at about 200 °C and shows the efficiency up to 85%.

4. Molten Carbonate (MCFC): These cells use a mixed alkali-carbonate molten salt electrolyte and operate at about 600 °C. They are being developed for continuously operating facilities, and can use coal-based or marine diesel fuels.
5. Solid Oxide (SOFC): These cells use a solid oxygen-ion-conducting metal oxide electrolyte. They operate at about 1000 °C, with an efficiency of up to 60%. They may find application in industrial and large-scale applications.

2. Results and Discussions

The catalytic properties of simple metals with respect to the system H₂-O₂ have been investigated experimentally for the long time in detail. Pt and Pd show the best catalytic activity (CA), as it is well known. The general theory of catalytic processes is developed rather poorly, as it is well known too. However, numerous experimental data point to a strong dependence of material CA on the processes of reagents adsorption and products desorption (Fig. 1) [1].

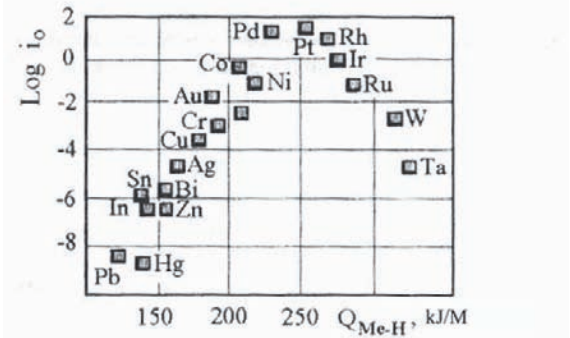


Figure 1. A correlation between the exchange current of hydrogen ion reduction and a bond energy (Q Me-H).

Some new catalysts for the reaction of the electrochemical hydrogen oxidation and oxygen reduction both from the groups 1 and 2 are presented below.

2.1. HYDROGEN OXIDATION CATALYSTS

The well - known anodic reactions of hydrogen oxidation in fuel cells are following:

- (1) $H_2 \rightarrow 2 H^+ + 2 e^-$ (in acid electrolyte)
- (2) $H_2 + 2 OH^- \rightarrow 2 H_2O + 2 e^-$ (in alkaline medium)

2.1.1 Non-noble metal catalyst (Table 1)

TABLE 1. Perspective non- precious metals catalysts for hydrogen oxidation

Catalyst	Method of preparation	Literature
Molybdenum carbide	gas-phase deposition	[3]
Tungsten carbide (WC)	- // - // - // - // -	[2, 3]
Radicals of following composition: -OH, -OSO ₃ H, -COOH, -OPO(OH) ₃	plasma treatment of gas diffusion layer	[4]
Allochromatium vinosum [NiFe]- hydrogenase	graphite supported adsorption Ni-Fe layer	[5]
Cr-Ni, La-Ni, Ti-Ni, Fe-Ni, Cu-Ni	deposition of respective metals on Raney nickel	[11]

New catalysts of hydrogen oxidation for low-temperature fuel cells are molybdenum and tungsten carbides [2, 3]. For solid polymeric fuel cells the novel catalysts by plasma treatment of polymer membrane have been developed. The radicals at surface are generated. These radicals are catalysts of anodic reactions [4] (Table 1).

Among the other metal catalysts for hydrogen oxidation, the *Raney nickel* deposited on the surface of graphite is widely known [10, 13]. The modification of Raney nickel with such metals like *Fe, Cr, Cu, La, Ti* has been proposed [11] with the aim to increase its effectiveness. The effectiveness of the doping metals follows the series: *Cr>La>Ti>Cu>Fe*.

2.1.2 Catalysts with the reduced noble metal content (Table 2)

To reduce the noble metals content in the electrode and to increase the catalyst activity, the electrode preparation by deposition of *Pd, Ni, Bi and La* on the surface of *Pt/C catalyst* [6], as well as the deposition of *Ru and Mo on platinum* by pulse electrodeposition at appropriate potentials have been elaborated [7].

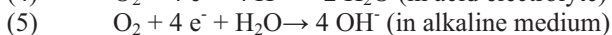
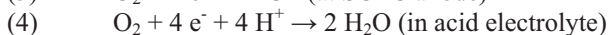
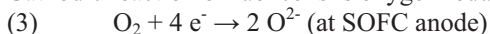
TABLE 2. Perspective noble metal catalysts for hydrogen oxidation

Catalyst	Method of preparation	Literature
Pt _x Ru _y and Pt _x Ru _y Mo _z	pulse electrolysis	[7]
Pd-Pt/C, Ni-Pt/C, Bi-Pt/C, La-Pt/C	deposition of Pd, Ni, Bi, La on the Pt/C catalyst	[6]
Cr-Ni, La-Ni, Ti-Ni, Fe-Ni, Cu-Ni	deposition of respective metals on Raney nickel	[11]
Pt-Pd/Au/C Pt-Ru/Au/C	deposition of sub-monolayers of Pt on Ru and Au nanoparticles supported by carbon materials	[12]
Pt/WO ₃ /C Pt-Ru/WO ₃ /C	Codeposition Pt and WO ₃ from solution by activated carbon	[28]

It is well-known that the presence of catalytic poisons (CO for example) in hydrogen gas exerts strong influence on the effectiveness and long-term stability of the electrodes containing Pt, Pd and other noble metals as a catalyst. The modification of this catalyst by such metals as Nb, Mo, Ta and Ru increased electrode life in presence of CO [8, 9]. Utilization of tungsten oxide (WO₃) jointly with Pt and Ru increase also electrode stability towards CO [28].

3. Oxygen reduction catalyst

Cathodic reaction of fuel cells is oxygen reduction.



The oxygen reduction begins on some step of reaction if pure catalyst is used. If catalysts are not good, the hydrogen peroxide is generated at some stages of electrode process. Hydrogen peroxide is very strong oxidizer and destroys the construction of the fuel cell. Therefore, the catalyst must provide four-electron mechanism of reaction. Such catalysts are showed in the Tables 3, 4.

3.1. NON-NOBLE METAL CATALYST (TABLE 3)

TABLE 3. Perspective non-precious metal catalysts for oxygen reduction

Catalyst	Method of preparation	Literature
Tungsten carbide (W_2C)	gas-phase deposition	[2, 3]
Co-polypyrrole complex	polypyrrole modification, deposited on carbon	[13]
Mixture of oxide Ni and Co	Vacuum deposition	[16]
Mn-polypyrrol-phthalocyanine complex	Electropolymerization	[14]
Co(II)-tetrasulphophtalo-phthalocyanine complex	Complex adsorption on SiO_2/TiO_2	[17]
$LaNi_{0.9}Fe_{0.1}O_3$, $La_{0.95}Sr_{0.05}Ni_{0.9}Fe_{0.1}O_3$	By ceramic technology	[19]
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ -CuO	- // - // - // -	[30]
MnO_x/C with ions Ca(II), Mg(II), Ni(II), Bi(III), Cr(III)	Reduction of $KMnO_4$ by carbon black	[15]

3.1.1. Conducting polymers (PANI, PPy and others as well as manganous oxides, perovskite and some other materials are used as non-noble metal catalysts.

Through examples of new catalyst of this class could be mentioned polymeric complexes such as Co-polypyrrole complex [13], Mn-polypyrrol-phthalocyanine complex [14], Co(II)-tetrasulphophtalophthalocyanine complex [17]. Active center of this catalyst is the metal ion encircled with nitrogen atoms. The structure of Mn-polypyrrol-phthalocyanine complex (MnTPhPyrPc) is showed in Fig. 2.

Modification by such ions like: Ca, Mg, Ni, Bi, Cr is proposed for improvement of manganous oxide catalyst [15]. The most effective modifiers are Ca(II) and Mg(II) ions.

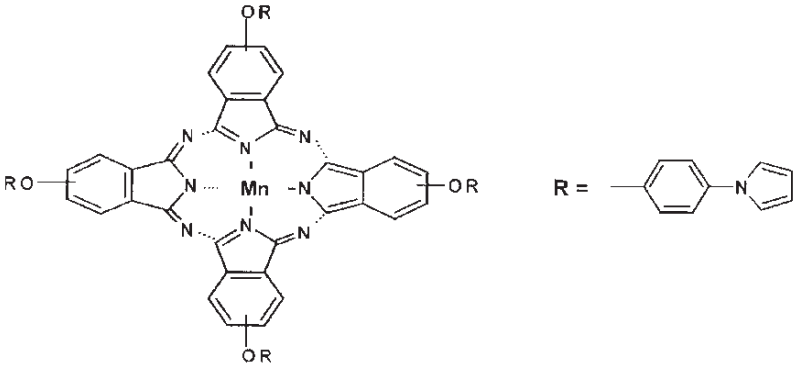


Figure 2. Structure MnTPhPyrPc.

3.1.2. Catalyst based on bioorganic substances

Interestingly that the bioorganic substances may be used in fuel cells as electrocatalysts. The new catalyst of hydrogen reactions is Allochromatium

vinosum [NiFe]–hydrogenase adsorbed on pyrolytic graphite [5]. Structure of Ni-Fe hydrogenase is showed in the Fig. 3. The effectiveness of this catalyst is comparable to the Pt catalyst.

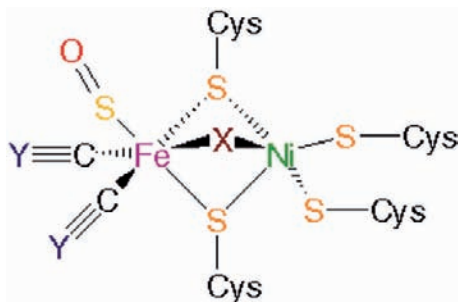


Figure 3. Structure Fe-Ni hydrogenase . X = S or O; Y = O or N; Cys = CYSTEINE.

The catalyst of oxygen reactions are derivatives of Vitamin B 12 [24]. These complexes contain an active sorption center, which consist of conjugated nitrogen atoms.

A mechanism of catalytic activity of electronically conducting polymers (ECP) of polyaniline (PANI) type was investigated in [26, 27]. To explain the reasons of the catalytic activity of ECPs, a quantum-chemical modeling of ECPs and adsorption complexes of ECPs with oxygen has been performed. The catalytic activity takes place due to the unique electronic structure of ECPs. The calculations showed that the bond orders in chemisorbed oxygen molecules at PANI decrease by one third, and the bond length increases by more than 20% in comparison with that in a free oxygen molecule. Thus, chemisorbed oxygen molecules have a fairly high degree of activation and can be readily reduced at the polymeric surface (Fig. 4). The similar mechanism takes place on the active carbon atoms of PPy, PT, PMeT.

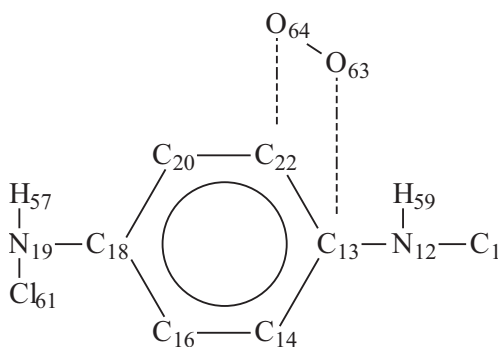


Figure 4. “Bridge model” of oxygen adsorption on PANI.

3.1.3. Catalysts with reduced content of the noble metal (Table 4)

Combinations of platinum catalyst and Fe-tetraphenylparpherine complex increased the efficiency of oxygen reduction [21]. The decay product of methanol in DMFC

decreased cathode efficiency for noble catalysts. Following catalysts are developed for DMFC: $\text{Os}_x(\text{CO})_n$ -Pt/C [28], CeO_2 -Pt/C [27], Fe-tetraphenylporphyrin- Pt/C [26].

TABLE 4. Perspective noble metal catalysts for oxygen reduction

Catalyst	Method of preparation	Literature
Deposition of derivative Vitamin B12 on Au	Spontaneous process on particles Au	[24]
Fe-tetraphenylparphrine-Pt/C	–	[21]
CeO_2 -Pt/C	Deposition of CeO_2 on Pt/C	[22]
Pt-Ni/C, Pt-Co/C	Deposition Ni, Co, on Pt/C	[20]
$\text{Os}_x(\text{CO})_n$	Pyrolysis of $\text{Os}_x(\text{CO})_n$ at 180°C	[23]

4. Multi-functional catalysts

Interesting direction in the field of investigations of catalysts is the development of multi-functional catalysts that catalyse both the anodic hydrogen oxidation, as well as the cathodic oxygen reduction reactions. These catalysts are prepared mostly basing on noble metals. One of such catalysts is the material obtained by deposition of a monolayer of Pt on Pd and Au nanoparticles, deposited on the surface of high-purity carbon material [12]. Such catalyst increases the activity of electrode by 3-4 times in comparison with the commercial samples. The deposition of $\text{Pt}_{0.75}\text{Pd}_{0.25}$ monolayer on the gold particles distributed on carbon matrix allow to increase the catalytic activity of the oxygen reduction reaction 2.5 times in comparison with typical Pt catalyst.

The tungsten carbides (WC and W_2C) has also attracted attention. The WC is catalyst of hydrogen oxidation, the W_2C is catalyst of oxygen reduction. The technology of WC and W_2C preparation is identical.

The catalysts for oxygen reduction and oxygen oxidation are materials based on substances like Co, Ni, Fe, Mn [16, 19]. One of new applications of oxygen reduction catalysts is air-metal hydride accumulator. Electrodes based on $\text{La}_{0.1}\text{Ca}_{0.4}\text{CoO}_3$, $\text{La}_{0.1}\text{Ca}_{0.9}\text{MnO}_3$ [18] are used in this battery. The electrodes of similar composition could be used in SOFC. An insertion of the oxides in their composition (CuO for example) leads to increasing the conductivity of system and efficiency of catalyst [30].

5. Conclusions

It is possible to mark the following promising materials for the two main groups of catalysts:

Grope 1. Non-platinum catalysts:

For hydrogen oxidation: bi-component metal doped systems deposited on Raney nickel for AFC; Mo and W carbides for AFC prepared by method of precipitation from a gas phase; Radicals of following composition: $-\text{OH}$, $-\text{OSO}_3\text{H}$, $-\text{COOH}$, $-\text{OPO}(\text{OH})_3$ for PEMFC; Some organic catalysts like biologically active $[\text{NiFe}]$ -hydrogenase, pyropolymers, etc.;

For oxygen reduction: N4-organic metal complexes and conducting polymers, transition metals oxides, perovskites, etc.

Grope 2. Catalysts with reduced Pt, Pd content on carbon (ceramic) support:

For hydrogen oxidation: bi-component Pt-Me/C catalysts (with the best results for Pt-Pd/C); three-component Me-Pt-Pd/C catalysts (with the best results for Ni-Pt-Pd/C); Pt-Ru/C and Pt-Ru-Mo/C catalysts; Pt-Pd/Au/C and Pt-Ru/Au/C catalysts;

For oxygen reduction: composites of N4-organic metal complexes and noble metal catalyst, bi-component Pt-Me/C (with the attained best result for Ni-Pt/C).

All above mentioned catalysts were developed taking into account the synergetic effects. That is why their further optimization needs finding the effective combination of different catalysts.

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DESCRIPTION OF PHASE EQUILIBRIUMS IN INTERMETALLIC COMPOUNDS WITHIN THE PERTURBATION THEORY

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Abstract. A phase equilibria in intermetallic compounds hydrides in the area of disordered α -, β -phase in the framework of the model of non-ideal lattice gas are described. LaNi_5 hydride was chosen as the subject for the model verification. Position of the critical point of the $\beta \rightarrow \alpha$ -transition in the LaNi_5 -hydrogen system was definite.

Keywords: Hydrogen, metal hydrides, intermetallic compounds, phase equilibria, model of non-ideal lattice gas.

1. Introduction

Application of intermetallic compounds (IMC) as working substances for thermo sorption compressors, thermal pumps, systems for hydrogen storage, purification and enrichment of hydrogen is motivated first of all by the fact that IMC hydrides possessing high sorption capacity are formed under rather mild thermodynamic conditions (even at the temperatures of about room temperature and at relatively low hydrogen pressures). The paper is devoted to description of phase equilibria in IMC hydrides in the area of disordered α -, β -phase in the framework of the model of non-ideal lattice gas. As the subject for investigation LaNi_5 hydride was chosen. Position of the critical point of the $\beta \rightarrow \alpha$ -transition in the LaNi_5 -hydrogen system is of a special interest because experimental data on its parameters are absent.

2. Model of the lattice H-gas for IMC hydrides

Our approach to the problem of calculations of phase equilibria in metallic hydrides [1] lies in determination the properties of hydrogen subsystem of a metallic hydride, and also of H_2 molecular phase that is in equilibrium with the subsystem in the frameworks of unified methods – modified scheme of perturbation theory (MPT) [2]. Thermodynamic description of the hydrogen subsystem in the area of disordered phases is performed on the basis of the model of non-ideal (interacting) lattice gas of hydrogen atoms. With that both direct interaction between hydrogen atoms and indirect “deformation” contributions to potential energy due to the lattice widening with hydrogen solution are taken into account.

In the present paper we are going to generalize the method for calculation of the phase α – β equilibria in the metal hydrides [3] for the IMC hydrides.

We will notice the following important circumstance: in the area of disordered α - β phases, initial IMC crystal structure in the most instances does not differ from the structure of the metallic matrix in the hydride phases in IMC-hydrogen systems. In this case chemical potential $\mu_H = G_H/N_H$ of the hydrogen component of the IMC hydride (that is, specific, per H atom, Gibbs energy G_H) is as follows:

$$\beta\mu_H^+(\theta, T) = \ln \frac{\theta}{1-\theta} + \frac{W_1\theta}{T(1+\alpha c_s\theta)} + \frac{W_2\theta^2}{T^2(1+\alpha c_s\theta)^2}, \quad (1)$$

where $\beta = 1/kT$; $\mu_H^+ = \mu_H - \mu_H^{st}$; $\mu_H^{st}(T)$ - chemical potential in standard state [1]; $\theta = C/C_s$ - relative hydrogen concentration; $C = n_{IMC}c$ - hydrogen concentration in the form of H/IMC relation, that is per formula unit of IMC; n_{IMC} - number of atoms in formula unit; c - H concentration in H/Me units, that is per an atom of matrix; $\alpha = c-I(\Delta V(c)/V)$ - dilatation coefficient of IMC lattice with hydrogen solution. Magnitudes C_s [H/IMC] - IMC sorption capacity, or the maximum number of the interstitial positions of H atoms in the phase area being studied, and c_s [H/Me] - the maximum concentration c related by the $C_s = n_{IMC}c_s$ relation.

W_1 and W_2 constants providing relation between macroscopic properties of the interstitial solution IMC-hydrogen and microscopic (atomic) characteristics of the hydrogen subsystem and IMC metallic matrix are equal:

$$W_1 = 2 I_1 n_M (\sigma_1^3 / v_0) E_1 c_s; \quad W_2 = (3 I_2 / 4 I_1^2) W_1^2, \quad (2)$$

where $I_1 = -5.585$, $I_2 = 1.262$ - MPT parameters for H-gas [1], n_M - number of the matrix atoms in the elementary cell; v_0 - the cell volume at $C=0$; E_1 [K] and σ_1 [m] - parameters of the $u_H(r) = kE_1\phi(r/\sigma_1)$ - potential of (H-H)-interaction.

3. Phase equilibriums in the LaNi₅ - H₂ system

We will discuss the phase equilibriums in LaNi₅ IMC hydride in the area of disordered phases. For binding LaNi₅ with the hexagonal structure of CaCu₅ type with the parameters $a_0 = 5.015 \cdot 10^{-10}$ m, $c_0 = 3.987 \cdot 10^{-10}$ m [4] of the elementary cell containing $n_M = n_{IMC} = 6$ atoms, its volume $v_0 = 86.84 \cdot 10^{-30}$ m³. In the area of α - β -equilibriums which is of the interest from the practical viewpoint under mild thermodynamic conditions (pressures up to $\sim 10^3$ atm) when mostly T - interstices are occupied the value of $C_s = 6.7$ ($c_s=1,12$). According to [5] we have for the dilatation coefficient $\alpha \cong 2.9 \cdot 10^{-30}$ [m³], $n_M/v_0 = 0.20$.

The $E_1\sigma_1^3$ combination in (2) is responsible for power component of (H-H)-interaction in the IMC lattice. As it is estimated from [6, 7] for LaNi₆ is 40-50% from the interaction constant of H-atoms in singlet states (the model for Pd hydride [1]); we will set $E_1\sigma_1^3 = 0.45(E_1\sigma_1^3)_{Pd}$; that gives $W_1 = -2.52 \cdot 10^3$ K, $W_2 = 1.93 \cdot 10^5$ K².

The phase diagrams relating the p_{H_2} pressure of the H₂ gaseous phase with the hydride parameters c and T may be obtained from the equality condition of $\mu_H(c, T)$ chemical potentials of H subsystem of hydride and $\mu_{H_2}(p_{H_2}, T)$ potential of H₂-phase calculated per H atom:

$$\frac{1}{2} \mu_{H_2}(p_{H_2}, T) = \mu_H(c, T) \quad (3)$$

If with the specified values of c and T decomposition of nonstoichiometric hydride (IMC) H_β occurs in α -solid solution (IMC) H_α and H_2 , in the PCT-diagrams intervals of constant pressure (plateau) $p_{H_2}^{(PL)}(T)$ appear in the $(\alpha+\beta)$ double-phase area; their position can be defined from the equality [5, 8]

$$\frac{c_\beta - c_\alpha}{2} \beta \mu_{H_2}^{(PL)} = \beta (h_{MH}^{(\beta)} - h_{MH}^{(\alpha)}) - (s_{MH}^{(\beta)} - s_{MH}^{(\alpha)}) \quad (4)$$

where $\mu_{H_2}^{(PL)} \equiv \mu_{H_2}(p_{H_2}^{(PL)}, T)$ - H_2 chemical potential at the plateau; $\beta h_{MH}^{(x)} \equiv H_{MH}(c_x, T) / RT$, $s_{MH}^{(x)} \equiv S_{MH}(c_x, T) / R$ - specific enthalpy and entropy of the hydride at phase boundaries $c_x(T) = c_s \theta_x(T)$, which are determined with equal areas rule [3].

With three-phase $(\alpha+\beta+H_2)$ equilibrium besides the condition of $\mu_H^+(\theta)$ equality at the boundaries of α - and β -phases, the $\mu_{Me}^{(\alpha)} = \mu_{Me}^{(\beta)}$ [8] equality is also true. After transformation of the equations (3) and (4) for $p_{H_2}(\theta, T)$ curves intersecting single- and double-phase areas of IMC hydrides we will obtain:

$$\ln p_{H_2}(\theta, T) = \ln p_{H_2}^{(PL)}(T) + 2\beta[\mu_H^+(\theta, T) - \mu_H^{+(PL)}(T)] \quad (5)$$

where $\mu_H^{+(PL)}(T)$ - is the height of the plateau at concentration dependencies of $\mu_H^+(\theta)$ isotherms that is determined by conditions of the gas-liquid phase transition in the hydrogen component of the hydride i.e. in the lattice H-gas [3].

Pressure of the β -phase decomposition, that is, the height of the corresponding pressure plateau $p_{H_2}^{(PL)}(T)$ specific for $\beta \rightarrow \alpha$ phase transition can be presented as Van't-Hoff equation:

$$\ln p_{H_2}^{(PL)}(T) = -\frac{\Delta H_{\beta \rightarrow \alpha}}{RT} + \frac{\Delta S_{\beta \rightarrow \alpha}}{R} \quad (6)$$

where the physical meanings of $\Delta H_{\beta \rightarrow \alpha}$, $\Delta S_{\beta \rightarrow \alpha}$ parameters depending on temperature are enthalpy and entropy of $\beta \rightarrow \alpha$ transition. Their formal expressions coincide with those obtained before [3] for Pd hydride:

$$\Delta H_{\beta \rightarrow \alpha} \cong H_{H_2}^0 + 2RT\Delta_{\beta \rightarrow \alpha}; \quad \Delta S_{\beta \rightarrow \alpha} \cong S_{H_2}^0 - 2R\Delta_{\beta \rightarrow \alpha} \quad (7)$$

However, in the case of IMC hydrides $\Delta_{\beta \rightarrow \alpha}$ parameters should be redefined again due to incorrectness of approximations [3] that were used for lattice H-gas in Pd-hydride. That is connected with the fact that the maximum density of the hydrogen subsystem $\rho_H(c)$ in the β -phase of $LaNi_5$ hydrides ($c_s = 1.12$) is twice as high as of PdH_β ($c_s = 0.6$).

Together with this task, a task arises of findings $\Delta H_{\beta \rightarrow \alpha}$, $\Delta S_{\beta \rightarrow \alpha}$ that are constant over the operating temperature range because the convenience of application of conventional equation (6) is connected with this fact. It is sufficient to use these parameters at some fixed temperature T_0 [3]; the only isolated point in area being studied is critical point of $\beta \rightarrow \alpha$ - transition, $T_0 = T_c$. Changing from (4) to (5) gives for parameter $\Delta_{\beta \rightarrow \alpha} = \Delta_{\beta \rightarrow \alpha}(T_c)$:

$$\Delta_{\beta \rightarrow \alpha} = -[(\theta \beta h_H)' - (\theta s_H)] = -(\theta \beta \mu_H^+)' = -\beta \mu_H^+(\theta_c, T_c), \quad (8)$$

as in the critical point $(\mu_H^+)' = 0$. Here $(...)'$ means the derivative in θ at $\theta = \theta_c$, $T = T_c$; h_H and s_H – excess values of enthalpy and entropy of the lattice H-gas [1]. Such choice of the fixed point T_0 according to (7), (8) and taking into consideration that [3]

$$\beta \mu_H^{+(c)} = \beta \mu_H^+(\theta_c, T_c) = -2,15 - \ln(1 + \alpha c_s), \quad (9)$$

gives analytical expressions for the constant parameters $\Delta H_{\beta \rightarrow \alpha}$, $\Delta S_{\beta \rightarrow \alpha}$ in Van't-Hoff equation (6), that is, for enthalpy and entropy of $\beta \rightarrow \alpha$ – transition which do not depend on the lower boundary of operating temperature range.

4. Results and Discussion

According to (9), parameters of the critical point of $\beta \rightarrow \alpha$ – transition in LaNi_5 hydrides: temperature $T_c = -0.216W_1 / (1 + \alpha \cdot c_s) = 445$ K, concentration $C_c = \theta_c \cdot C_s = 2.75$ H/ LaNi_5 ($\theta_c = 0.46 / (1 + 0.54\alpha \cdot c_s) = 0.41$). Having defined $H_{H_2}^0(T_c)$, $S_{H_2}^0(T_c)$ – values of enthalpy and entropy of H_2 in the state of ideal gas at $T = T_c$ according to [10] and taking $\Delta_{\beta \rightarrow \alpha} = 2.3$ according to (7) and (8) we will find the

following parameters of the Van't-Hoff equation: $\Delta H_{\beta \rightarrow \alpha} = 29.8$ kJ/mole H_2 , $\Delta S_{\beta \rightarrow \alpha} = 104$ J/(K·mole H_2). The calculated data on the pressure of decomposition of

LaNi_5 β -phase in the temperature range from 263 K to the critical temperature are compared in the Fig. 1 with the experimental data [11, 12] on hydrogen desorption; the experiments were carried out in limited temperature ranges.

The phase diagram of the LaNi_5 – H_2 system in the form a set of isotherms of hydrogen solubility is calculated at the temperatures below T_c from the expression (5), and in overcritical single phase area $T \geq T_c$ with the method presented in the paper [3]. The computer code created for calculating phase equilibriums in IMC hydrides in the area of disordered phases was based on determination of the boundaries of α - and β -phases (the decomposition curve of homogenous phase) and the following calculations of $P_{H_2}(C, T)$ in the single phase areas α and β according (5) and (6) (falling and rising branches of the isotherm) and position of the pressure plateau $p_{H_2}^{(PL)}(T)$ in the double phase area $\alpha + \beta$. The obtained results are presented in the Fig. 2 in comparison with the experimental isotherms of hydrogen desorption [12].

At the temperature T_c according to (6) H_2 pressure at the critical point is $P_{H_2}^{(c)} = 87$ atm. Values of the critical parameters $T_c = 445$ K, $C_c = 2.75$ H/ LaNi_5 , $P_{H_2}^{(c)} = 87$ atm (experimental data on them are absent) which were obtained above for $\beta \rightarrow \alpha$ – transition much better agree with the shape of phase diagram in this area of states than the values $T_c = 450$ K, $C_c = 3.3$ H/ LaNi_5 and $P_{H_2}^{(c)} \sim 200$ atm that were obtained in paper [13] in framework of crude model – Bragg-Williams approximation for rigid lattice ($C_c = 0.5C_s$).

The results given in Figs. 1 and 2 shows that application of thermodynamic perturbation theory for simulating phase equilibria in IMC hydrides gives, mainly, correct description of the main peculiarities of the PCT diagrams of the $\text{LaNi}_5\text{-H}_2$ system in the area of disordered phases over the wide pressure range.

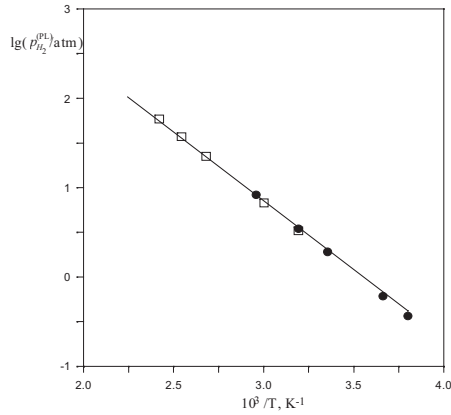


Figure 1. Logarithm of pressure of β -phase decomposition $\ln P_{H_2}^{(PD)}$ for LaNi_5 versus inverse temperature T , K 1: — calculation according to (6) at $\Delta H_{\beta \rightarrow \alpha} = 29.8$ kJ/mole H_2 , $\Delta S_{\beta \rightarrow \alpha} = 104$ kJ/mole H_2 ; $\square$ [11]; $\bullet$ [12] – experimental data on desorption in the $\text{LaNi}_5 - \text{H}_2$ system.

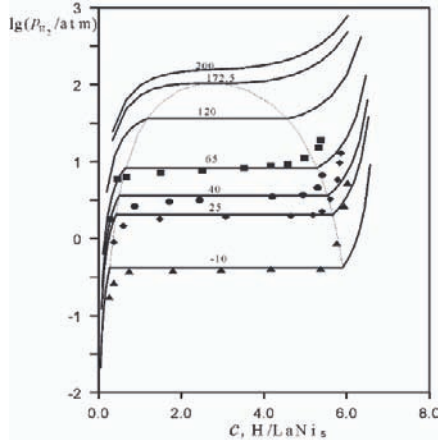


Figure 2. Isotherms of hydrogen solubility $P_{H_2}(C)$ of LaNi_5 according to (5) ($T < T_c$) and calculation scheme [3] ($T \geq T_c$). Temperatures at calculated isotherms are given in $^{\circ}\text{C}$. Dotted curve - calculated boundaries of single- and double- phase areas in ($\lg P_{H_2} - C$) plane. Experimental data on desorption [12] at the temperatures, $^{\circ}\text{C}$: - 10, 25, 40, 65.

The subject for further investigations in frameworks of proposed method for calculation of phase equilibria is description of equilibrium isotopic effect in intermetallic hydrides; the method is used for isotope isolation and hydrogen

enrichment. Inversion of isotopic effect observed at the ambient temperature in the LaNi_5 system is also of a great interest.

5. Conclusion

Application of the model of the non-ideal lattice gas of H-atoms for description of phase equilibriums in IMC hydrides allows reproducing main peculiarities in the phase diagrams of the IMC - hydrogen systems in the area of disordered α - and β -phases. For LaNi_5 hydrides isotherms of solubility of hydrogen obtained for a wide pressure range agree well with the experimental data. Position of the critical point of the $\beta \rightarrow \alpha$ transition in LaNi_5 system was determined.

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MgH₂–CARBON COMPOSITES FOR HYDROGEN STORAGE

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Abstract. Peculiarities of hydrogenation reactions of magnesium at temperatures of 410°C to 450°C and pressures of 15 to 55 MPa have been investigated. Interactions in MgH₂–graphite system under quasihydrostatic conditions (3 GPa, 800°C, 1 h) have been explored. It has been shown that such a treatment did not lead to formation of new chemical compounds. The phase transformation of MgH₂ to a metastable high-pressure modification has been found. As a result of mechanochemical activation, the MgH₂–graphite and MgH₂–CNF composites have been obtained. It has been pointed that the mechanical activation of mixtures of magnesium hydride with carbon affect strongly the kinetic parameters of hydrogen desorption but also led to decreasing the thermal stability of the hydride phase.

Keywords: Magnesium hydride; Graphite; Mechanochemical treatment; Composite; Hydrogen storage

1. Introduction

It is well-known that magnesium and its alloys are promising materials for hydrogen storage due to high capacity of forming hydrides and reversibility of hydrogen sorption/desorption process. However, slow hydrogenation reaction and high temperature of hydrogen release (more than 300°C) put obstacles on the way of magnesium use for hydrogen storage. The present investigation is devoted to the development of magnesium modification methods which should allow improving the kinetics and decreasing the temperature of dehydrogenation.

The most interesting method for improving kinetics of magnesium interaction with hydrogen is mechanical activation leading to high concentration of defects and increase of active surface. In the case of magnesium hydride based systems mechanochemical activation results in a appreciable improvement of the hydrogenation rate [1]. Hopeful results have been obtained in [2] where mixture of magnesium with graphite was ball milled. Hydrogenation of such composites has been realized at temperature of less than 200°C and thermodesorption peak has been shifted into area of lower temperatures.

In the present work magnesium hydride as a starting material has been used for higher effectiveness of mechanochemical treatment. Magnesium hydride is less plastic and more fragile material as compared with metallic magnesium [3].

2. Experimental

Magnesium 99.9%, hydrogen 99.9999%, graphite 99.99% have been used as starting materials. Magnesium powder of weight 1.6–1.8 g has been prepared for the synthesis MgH_2 by mechanical size reduction.

The synthesis of MgH_2 has been carried out using high gaseous pressure technique at temperature 400–500°C and at the hydrogen pressure 15–55 MPa.

Mechanical activation was performed in a high energy (acceleration up to 70 g) planetary ball mill with stainless steel reactor and balls under an argon atmosphere during 1 h. All the sample handling has been operated in Ar-filled glove box (MBraun), in which the water/oxygen levels were below 1 ppm.

Thermal decomposition of samples has been made by the method of prolong exposure at constant temperature on installation of high gas pressure. Specific surface of the samples has been measured by the BET method with accuracy $\pm 10\%$ on device Autosorb-1 (Quantchrome, USA). X-ray powder diffraction data have been obtained with $\text{Cu K}\alpha$ radiation. Samples treatment under high quasihydrostatic pressures (3 GPa, 800°C, 1 h) has been done in the chamber of a high pressure.

3. Results and Discussion

Hydrogen-storage characteristics of samples of four types were studied: as synthesized MgH_2 (1), MgH_2 after mechanical activation, m/a (2); MgH_2 -graphite (3) and MgH_2 -carbon nanofibers (CNF) both after mechanical activation.

The process of interaction of magnesium powder with hydrogen under various pressures and temperatures was investigated in details and it was shown that: a) at 450°C the hydrogenation process started rapidly and reached the fractional conversion of 0.80–0.85 in 20–30 minutes, after that the rate of hydrogen absorption slowed down harshly; b) variation of hydrogenation temperature within the range of 300 to 500°C did not affect the fractional conversion, but influenced only on the rate of hydrogen absorption at initial stage of hydrogenation; c) increase in hydrogen pressure from 15 to 55 MPa caused an acceleration of absorption at initial stage of hydrogenation only.

The obtained results have shown that diffusion of hydrogen through the layer of formed hydride is the limit stage of process of magnesium hydrogenation.

In order to evaluate the phase relationships in the MgH_2 -graphite system a treatment of the mixtures under high quasihydrostatic pressures (3 GPa, 800°C, 1 h) has been done. As a result, formation of magnesium carbide nor graphite intercalation compounds were not detected. High pressure modification $\gamma\text{-MgH}_2$ has been found in the system treated. Besides that, preliminary mechanical treatment promoted the formation of this metastable high pressure modification.

It has been shown that mechanical activation led to substantial increase of specific surface of composites obtained in comparison with initial magnesium hydride and graphite (Table 1).

Figure 1 shows the results obtained under thermal decomposition of samples using the method of prolong exposure at constant temperature. As one can see, the pressure of hydrogen release from the samples at 150 and 250°C is higher after the mechanical activation as compared with non-treated powder of MgH_2 . This effect is much more pronounced for the samples with graphite.

TABLE 1. Specific surface of initial materials and composites obtained

Composition	Specific surface, m ² /g
Mg	0.1–0.2
MgH ₂	1.5–2
graphite	6–7
CNFs m/a	80–85
MgH ₂ m/a	7–8
MgH ₂ :graphite (1:1) m/a	60–65

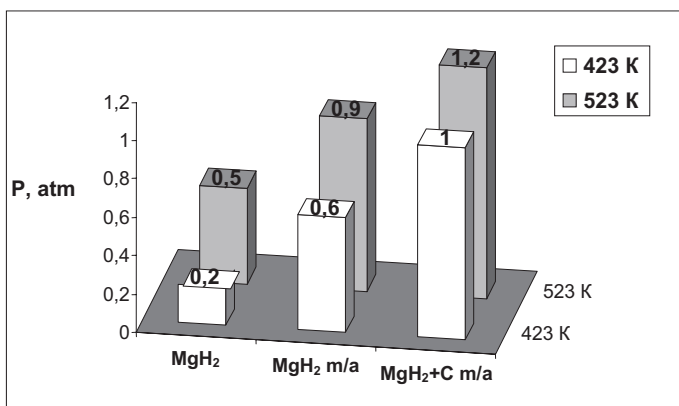
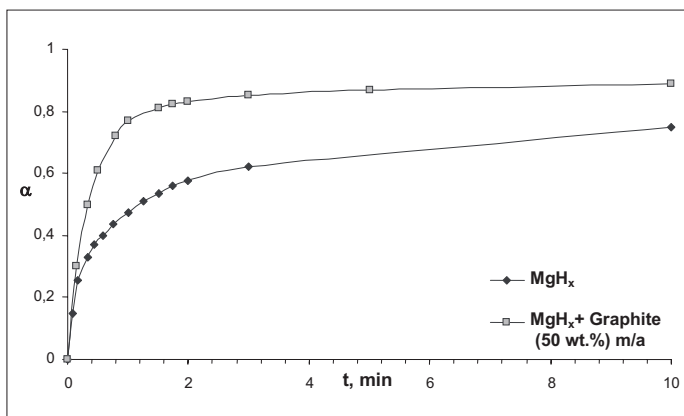


Figure 1. Desorption pressures at 150 and 250°C for the samples studied.

Hydrogenation of mechanically treated samples with graphite after the thermal decomposition led to the increase of the hydrogen sorption rate in comparison with magnesium produced during thermal decomposition of non-treated MgH₂ (Fig. 2).

Figure 2. The fractional conversion (α) of magnesium hydrogenation reaction at 330°C for samples after thermal decomposition.

The pressure of hydrogen released from samples with the smaller maintenance of a carbon phase (MgH_2 :graphite [25 weight %] and MgH_2 :graphite [10 weight %]) under thermal decomposition also essentially exceeds the pressure of hydrogen desorbed from the raw powder MgH_2 (Fig. 3). It is noted, that hydrogenation of these samples after the thermal decomposition led to increase of the hydrogen sorption rate (Fig. 4).

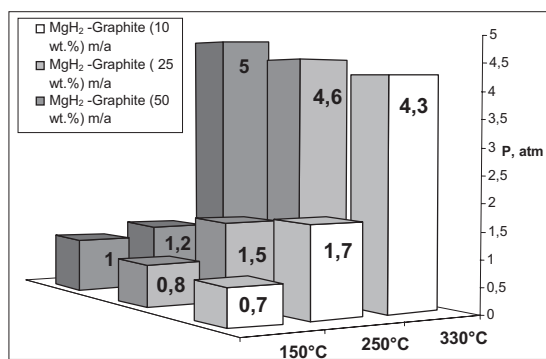


Figure 3. Desorption pressures at 150, 250 and 330°C for the samples studied.

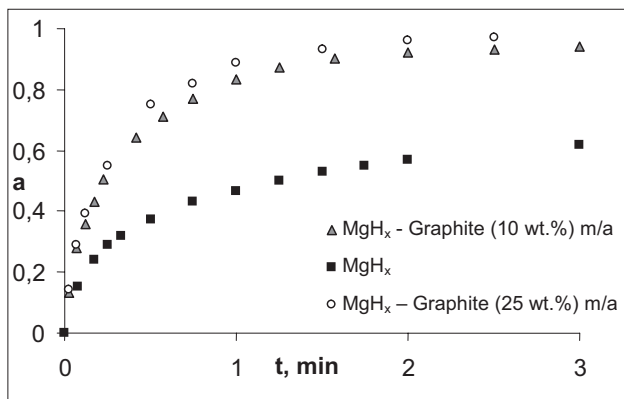


Figure 4. The fractional conversion (α) of magnesium hydrogenation reaction at 330°C for samples after thermal decomposition.

CNFs have been used as another carbon component for obtaining MgH_2 -C composites. The degree of amorphisation of composites obtained was substantially higher as compared with the MgH_2 -graphite composites. This is likely concerned the difference in the carbon component nature and their behavior during the treatment. The pressures of hydrogen release from such composites at the temperatures of 150 and 250°C were also higher than the desorption pressures of non-treated MgH_2 .

Acknowledgment

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SYNTHESIS OF CARBON NANOSTRUCTURES IN GASEOUS AND LIQUID MEDIUM

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Abstract. The advantages of arc synthesis in a liquid medium in preparing carbon nanostructures have been investigated. Changes in the chemical compositions of the reagents (electrodes and medium), the high temperature and pressure of the medium, the high rate of cooling and the growth of structures in the reaction zone allow materials with unique properties to be produced. The production of a purer product makes this productive method promising for the synthesis of carbon nanostructures for different applications.

Keywords: nanostructure, carbon nanotubes, arc discharge, plasma reactions, transmission electron microscopy.

1. Introduction

After the discovery of fullerenes and carbon nanotubes methods of their synthesis have been constantly investigated and improved.

In parallel with the arc method in gaseous phase and the pyrolytic method for synthesis of carbon nanostructures, since 2000 year the present group of researchers has been investigating and developing the method for arc synthesis in liquid phase. This method has a number of advantages over those used at present.

We have proposed the method of synthesis of carbon nanostructures and composites on their base by arc discharge in the liquid phase. In this connection the work on production of ultradispersed metal powders by the electroerosion method [1-4] began in the eighties years and still continues today. Besides carbon nanostructures produced by evaporation of carbon electrodes in the liquid phase, there appears a possibility of producing metal-carbon composites by sublimation of metal in the carbon-containing liquid. In this case the metal nanoparticles form with carbon nanostructures on their surface.

The main positive moments of the method used are:

1. High temperature in the arc zone > 4000 K.
2. High cooling rate of evaporated products $> 10^9$ K/s.
3. High dispersion level. The size of the particles produced is 1-100 nm.
4. High rate of nucleation at the low rate of the particle growth.

All these conditions have analogy with conditions for synthesis of fullerenes and nanotubes by the arc graphite evaporation in gaseous phase. The suggested method gives a possibility to produce a wide range of materials by changing the

conditions of synthesis. This method gives the possibility to modify the chemical composition both of electrodes and of medium, where synthesis is carried out. The liquid phase may have different chemical compositions that affect the structure and the composition of produced nanoobjects of inquiry (Fig. 1).

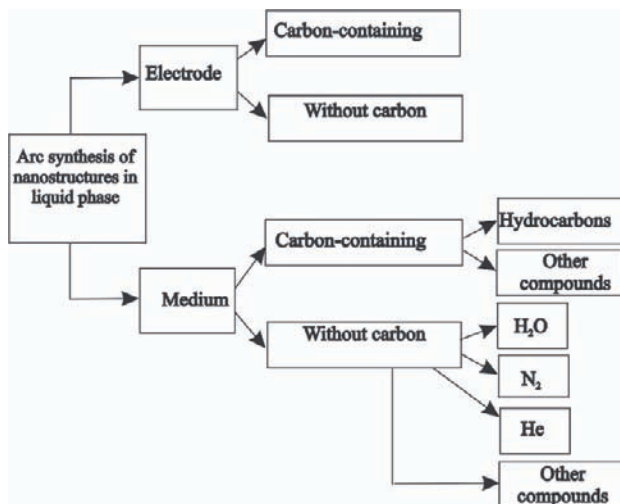


Figure 1. Scheme for possible combinations of medium and electrode materials in synthesis of nanostructures by the arc method in the liquid phase.

In the course of the experiments conducted in parallel with the described method the carbon nanostructures have been produced by pyrolysis of hydrocarbons and by arc evaporation of graphite in the gas phase in order to compare physical and chemical peculiarities of the formation of nanostructures and morphology of their structure.

It should be also noted that while the first method was applied earlier to produce different carbon pyrofibers and therefore it has been studied sufficiently, the second method of arc synthesis attracted a deserved attention of scientists as the method for synthesis of carbon nanotubes (CNT) only after Iijima's work has been published in 1991. This method requires the explanation of many unintelligible moments. Vagueness in understanding a mechanism of the nanotube growth hinders the progress in developing more controllable technologies for synthesis of these materials.

The present work is focused on the investigation of physical and chemical peculiarities in synthesis of carbon nanostructures and the effect of the cooling rate (i.e. the residence time of a carbon atom in the reaction zone) on peculiarities of the formation and morphology of the product. We have compared peculiarities of the formation of the nanostructures synthesized by pyrolysis, the arc method in the gas phase and the arc method in liquid in order to understand the effect of the earliest stages of nucleation on the further process of the nanostructure formation. All the methods are distinguished by the time of interaction between reagents.

In the course of the work we also have demonstrated the possibility of producing carbon nanostructures in the liquid phase (water, hydrocarbons,

dichloroethane, CCl_4 , in liquid gases). This method has not been studied sufficiently by the scientific community.

2. Experimental

Synthesis of carbon nanostructures by pyrolysis and arc discharge in the gas phase has been performed by the known methods. Synthesis in the liquid phase has been carried out on the installation designed specially for these studies (Fig. 2). This installation allows metal and graphite electrodes to be evaporated in the liquid medium at the temperature from 4 to 340 K using an electric arc. The arc temperature near a cathode may be as much as $1,2 \cdot 10^4$ K at currents of 200-300A (Fig. 3).



Figure 2. The installation for synthesis of nanocarbon structures and Me-carbon composites in the liquid phase.

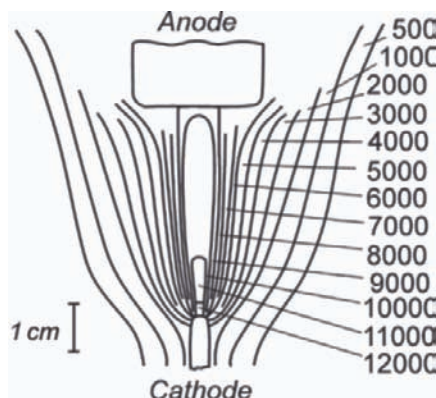


Figure 3. Temperature distribution (in K) in different parts of the electric arc between the carbon electrodes at strength of current equal to 200A [5].

The electronic control block is simple in operation and gives the possibility to vary and measure voltage and electric current. These changes in its turn allow the action on the conditions of the plasm-chemical process, that proceeds in the reactor, and the profound effect on the morphology and the yield of product.

All the chemical reagents used in synthesis have been subjected to preliminary purification and rectification. Graphite of MPG-7 grade has been used. The graphite rods have been annealed preliminary in vacuum. The metallic rods have been remelted repeatedly in an arc furnace in argon medium of spectral purity.

After synthesis the product has been washed with hydrocarbons with the use of ultrasound.

The synthesis products have been investigated using the scanning and transmission electron microscopy. The liquid phase has been studied by spectrophotometer and mass spectrometry (these results are not discussed in the present work).

3. Results and Discussion

The basic and uniting moment for all three methods employed for synthesis is the fact that the application of each of them requires the destruction of existing initial carbon and carbon-containing structure or compound (precursor) on atoms or groups of carbon atoms and then the preparation of new structure.

The variety in properties of different produced carbon materials is conditioned by the electronic structure of a carbon atom. The redistribution of electron density, the formation of electronic clouds of different modifications around the atoms, the hybridization of orbitals (sp^3 -, sp^2 -, sp - hybridization) are responsible for the existence of different crystalline allotropic phases and their modifications.

In the course of arc synthesis, when carbon atoms are supplied by sufficient amounts of energy, they pass from the graphite surface into the gas phase as separate atoms or groups of atoms. At the certain technological conditions they form the new carbon structure determined by synthesis conditions. As this takes place, the atoms spend the gained energy for the construction of this structure. The further existence of this carbon nanostructure, the conservation or the change of initial morphology and geometrical dimensions of a nucleus are determined by thermodynamical and technological conditions of its stay in one reaction medium or another.

In arc synthesis of carbon nanostructures in the gas phase two sorts of product form: 1) the soot on the reactor walls which contain different sorts of carbon nanostructures; 2) the product on the cathode which carry nanotubes and other structures. All the above-listed products formed in the course of this synthesis have different residence time of reagents in the reaction zone, all other things being the same. As temperature in the interaction zone changes at different rates, this causes the different time of nuclei holding in the reaction medium.

In the first case the rate of change (decrease) in temperature to the room temperature in the interaction zone is $1 \cdot 10^3$ K/s, and in the second case the rate of change to the temperature $\sim 1000^\circ\text{C}$ is more than $1 \cdot 10^5$ K/s.

The experiments have shown that with the pyrolytic method of synthesis, in spite of the high duration ($1 \cdot 10^4$ s) of technological process, CNTs are formed at the first moments of interaction and only after that they change their morphology and geometric dimensions. In this case it is of interest to consider the time of nanostructure formation and to know is it limiting at the arc synthesis or these structures are formed much more faster.

The arc synthesis of carbon nanostructures in the liquid phase was used to clarify precisely this problem because the residence time of product in the reaction zone (according [1-4]) is more than $1 \cdot 10^{-9}$ s. However, as it has been found later, the last method is sufficiently productive and less labor intensive as compared with already known methods. Moreover, in some cases the product can be formed in these conditions without catalyst involvement what simplifies the stage of product purification.

All products produced by three methods have similar morphology at the initial stage of the process. The morphology has undergone changes in the course of the further treatment of product. The synthesis time is one of the key moments in the nanostructure formation. The peculiarities of synthesis and morphology of some products produced by the arc method in the liquid phase are considered and discussed below.

a) Synthesis of nanostructures in hexane

The hollow nano-objects may be synthesized by the joint evaporation of carbon and a metal component in liquid. These nano-objects are formed when products get into the zone of high plasma temperatures repeatedly. This process may be presented as that proceeding in two stages. At the first stage a metal crystal with the more thermally stable surface film forms. At the second stage the product gets repeatedly into the zone of high temperatures (up to 12000 K) due to the turbulent movement of liquid with this product within the reactor (Fig. 3). This results in evaporation of metal from the thermally stable shell and formation of the nano-scaled hollow structure (Fig. 4).

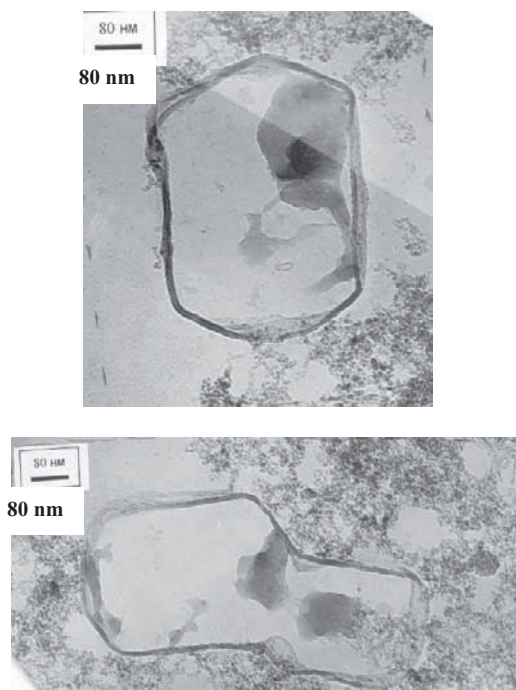


Figure 4. Hollow shells of nanocrystals.

b) Carbon nanostructures produced in distilled water

The carbon nanotubes up to 10-15 nm in diameter have been produced by the graphite evaporation in water. The resulting structures produced in water do not contain catalysts. This simplifies the process of their purification and reduces the net cost (Fig. 5). Varying the regime of synthesis one can produce both tubular and ribbon structures.



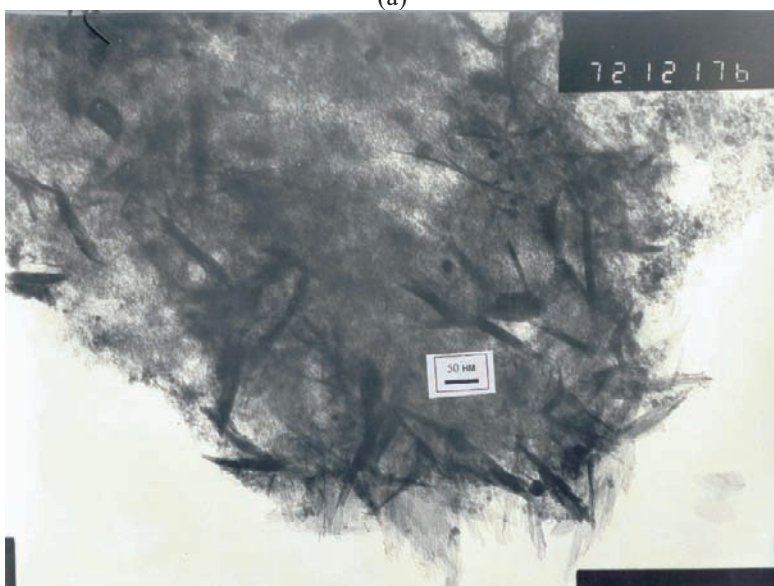
Figure 5. Carbon multiwall nanotubes produced by uncatalytic evaporation of graphite in distilled water.

c) Carbon nanostructures produced in liquid nitrogen

The sphere-like carbon structures are formed during the arc evaporation of carbon in liquid nitrogen (Fig. 6(a)) in joint evaporation of carbon and nickel, the different structures comprising the mixture of cotton-like carbon product and nickel needle-shaped structures are fabricated (Fig. 6(b)).



(a)



(b)

Figure 6. Carbon nanostructures produced in liquid nitrogen.

d) Carbon nanostructures produced in liquid helium

The product produced by the arc evaporation of graphite in liquid helium without additional purification contains up to 85-90% of carbon nanotubes. Such results are not always achieved using different methods for nanotubes purification (Fig. 7).

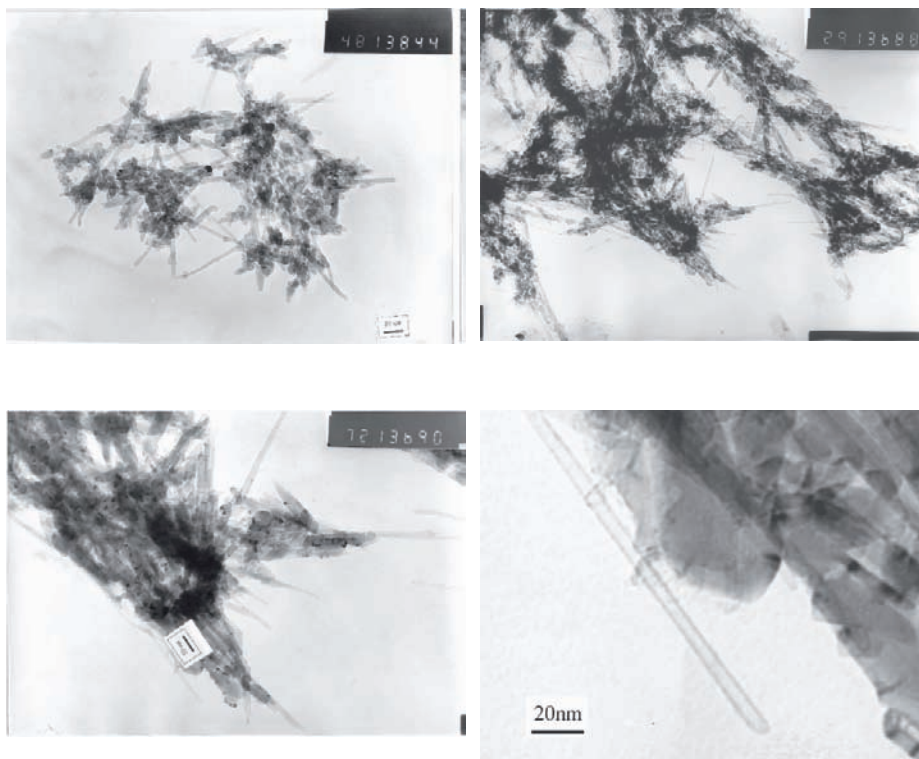


Figure 7. Carbon nanotubes produced in liquid helium (demonstrated without additional preparation: fragmentation, washing, extraction, purification etc.).

Different nano-objects can be synthesized under changes of the regime of synthesis and application of catalysts. In the course of synthesis the foamy particles (Fig. 8) are formed during the evaporation of highly dispersed graphite dust. Their conglomerates range up to 1-5 μm .

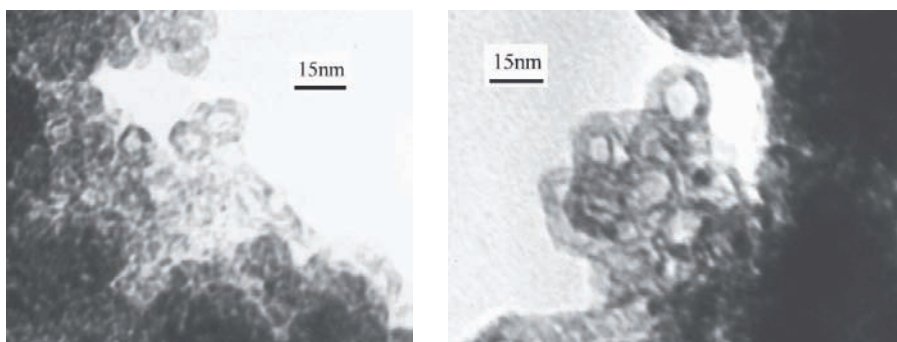


Figure 8. Carbon nanostructures produced in liquid helium.

e) Carbon nanostructures produced in chlorine-containing compounds

Nanostructures with different morphology (Figs. 9 and 10) and different volume fullness are formed during the graphite evaporation in chlorine-containing liquids.

The encapsulated nanotubes produced in dichloroethane are shown in Fig. 9. Their morphology and the volume structure completely correspond to the mechanism of the fast formation of a nanotube and its simultaneous encapsulation proposed in paper [6].

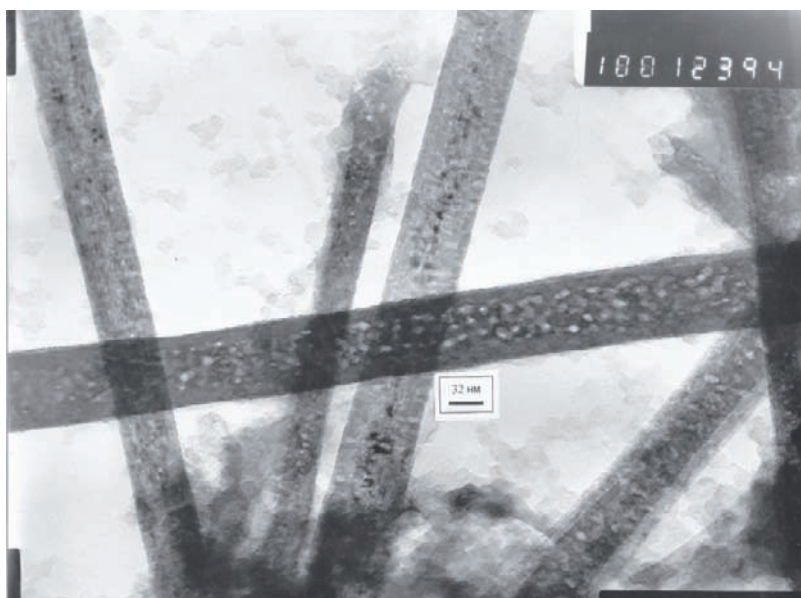


Figure 9. Carbon nanostructures produced in dichloroethane.

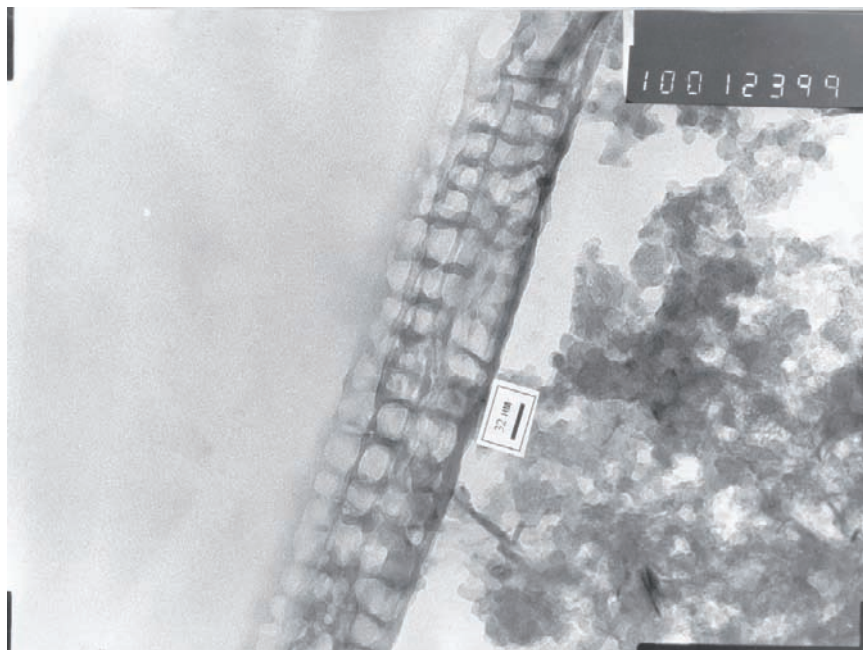


Figure 10. Carbon nanostructures produced in CCl_4 .

f) Synthesis of nanotubes from the fullerene solution in toluene

The original objects on the surface of nickel spheres have been produced in experiments with fullerene solutions [7-8].

As authors supposed from the generally accepted concepts of mechanisms of carbon nanotube growth, the dispersed nickel sputtered must catalyze the growth of these nanotubes. The source for carbon should be carbon from the hydrocarbon that transforms into the vaporous state in the arc zone. It has been supposed to prepare single-wall nanotubes on the nickel particles 1-10 nm in size and the layer of nanotubes up to 1 μm thick on the larger nickel particles.

The electron-microscopic studies have indicated that carbon nanotubes do not form on the nickel particles in the media chosen (alcohol, toluene, hexane).

However, when hydrocarbons with fullerenes mixed, carbon nanotubes up to 50 nm in diameter are formed on the surface of nickel microparticles. Nanotubes are not perpendicular to the surface (as in pyrolysis), but they are parallel to it. Tubes on the surface of particles form the continuous net (Fig. 11).

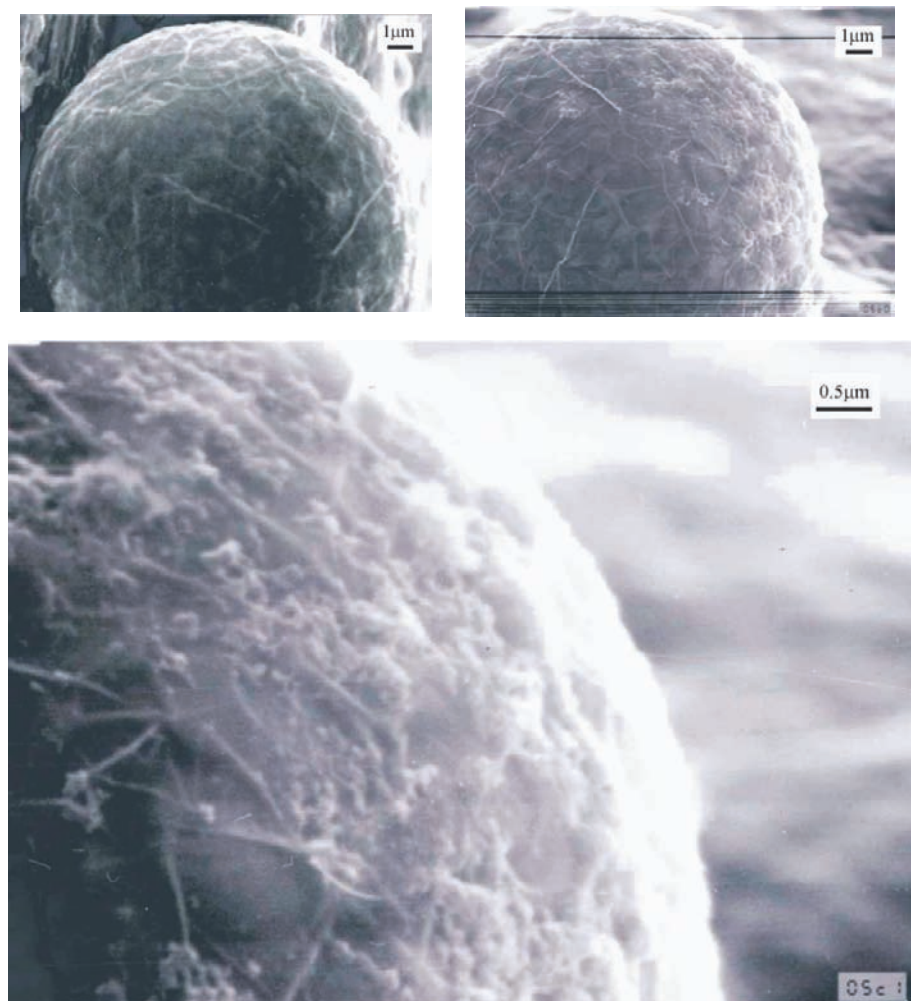


Figure 11. Carbon nanotubes on the nickel sphere surface.

Evidently, the dissolved fullerene molecules in toluene reaching the plasma zone with glowing nickel particles, undergo the crystallization and sublimation processes. These molecules become both nuclei and building material for the formation of carbon nanotubes of small and large diameters (>50 nm) on the surface of metallic spheres 15-30 μm in diameter (Fig. 11), forming the metal-carbon composite.

From the aforesaid, it might be assumed that the discussed method of carbon nanostructure synthesis is sufficiently productive. It allows the production of nanostructures and composites based on them with different morphology, different

properties and consequently for different applications. In this case during the reaction many carbon nanostructures, that are interpreted to be the by-product, have no time to form or grow because of a high rate of the temperature change.

The absence of the by-products enables the expenses on the product purification and consequently its net cost to be reduced.

The nanostructural carbon product (different multi-wall and single-wall carbon nanotubes (SWNT) and other structures) produced by three methods applied in this work has similar properties and morphology at the nano-level. According to the literature data and experimental results, the duration of the technological process (the residence time of a reagent in the reaction zone) of the carbon nanoprodukt synthesis by pyrolysis averages $1 \cdot 10^{-4}$ s, by the arc synthesis in the gas phase it is $1 \cdot 10^{-3}$ s and by the arc synthesis in the liquid medium the duration is more than $1 \cdot 10^{-9}$ s. For each of the methods the rate of the reagent transformation into a nucleus of product should not be different much, although the time of the technological cycle differs considerably for each method.

The difference in the duration of the technological process between the first and the last methods of synthesis is, on average, 13 orders. Experiments have shown that the transition from one method to another and the decrease in the interaction time do not have a significant effect on the nuclei morphology of the forming product, but affect considerably the product mass yield that mainly depends on the geometry of the objects formed in the end. At the first moment of interaction at the nano-level the nanostructural product, e.g. nuclei of a new molecular-sized structure, are formed. Hence the processes of the nanosecond duration, that determine the morphology and properties of the final product, should be given a special attention in the synthesis of nanostructural objects.

The technological chain of transformations, that are undergone by the initial carbon-containing reagents in the course of carbon nanostructure synthesis (by any of three methods), is shown in Fig. 12.

For synthesis of a new structure the reagents are produced by the method of destruction of carbon and carbon-containing precursor. The nuclei of certain carbon structure are formed during the interaction. Depending on the conditions of synthesis, the carbon structure may be carbene, fullerene, diamond, nanotube or other nanoobjects.

On holding the formed nuclei during some time in the certain technological conditions can cause the reconstruction of one structure to the another, the change of the morphology or the growth of nuclei and the yield of product in macro-amounts.

4. Conclusions

Based on experimental data and theoretical calculations we have attempted to consider the conditions and the mechanism of the processes proceeding in synthesis of carbon nanostructures.

The distinctive feature of the discussed method for nanostructural carbon material synthesis is that there is a possibility to produce these materials without catalysts owing to a very quick synthesis (competing with velocity of light). An example of such type of process is synthesis of carbon nanotubes by evaporation of pure graphite in liquid media.

If we consider the fact that during arc synthesis in the liquid phase the SWNTs are formed within nanoseconds, we can suppose that in pyrolysis of hydrocarbons the nuclei of CNTs should also appear sufficiently quickly. Their geometric dimensions vary within the rest of the time. Hence, using the holding time as a limiting factor (at all another equivalent conditions), one can synthesize the carbon nanostructures with the predetermined geometric dimensions. The process of SWNTs synthesis will be the fastest as this is a primary process, i.e. the process of nuclei synthesis. Affecting this process, one can form morphology and properties of the final product.

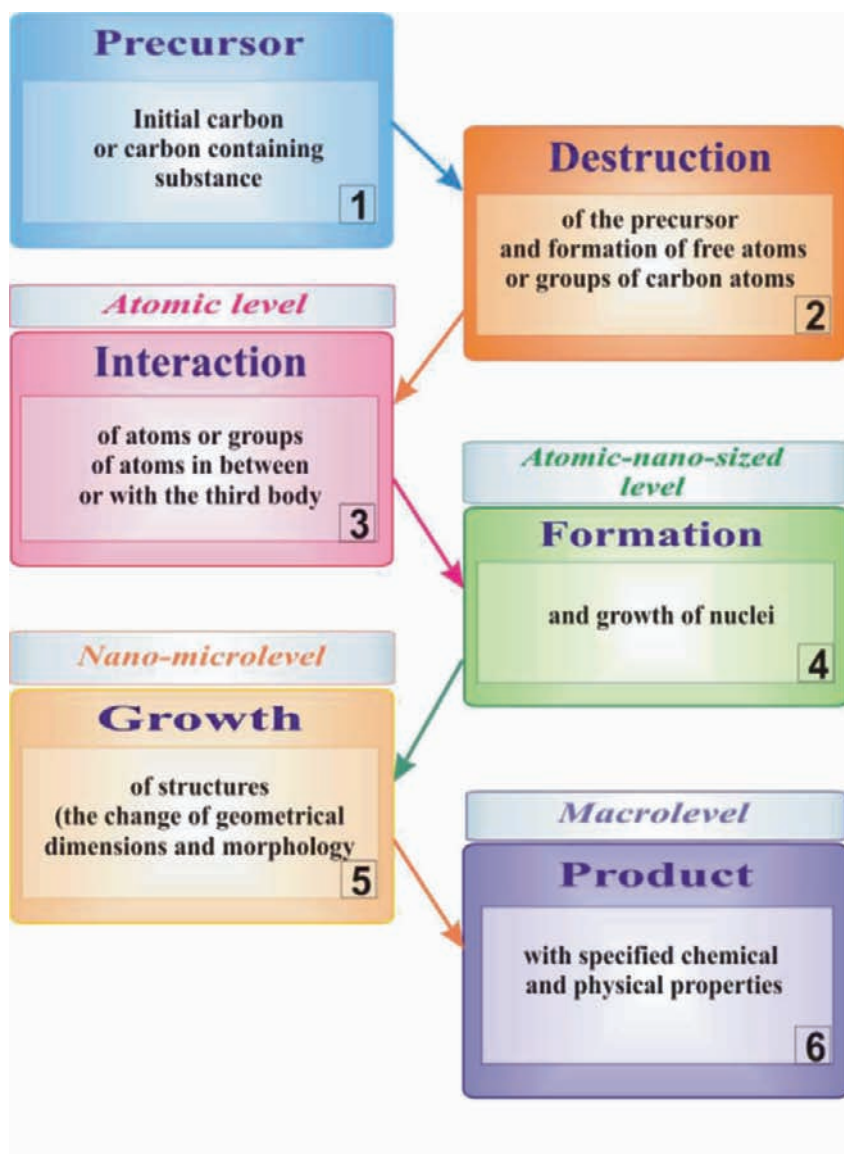


Figure 12. Technological chain of carbon structure formation.

All obtained results are of scientific and practical interest. The prepared materials require further investigations. The proposed method can be one of the most effective method to synthesize fullerenes and nanotubes.

Acknowledgements

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Pt NANOCCLUSERS ON CARBON NANOMATERIALS FOR HYDROGEN FUEL CELLS

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Abstract. The detailed study of carbon nanomaterials constitution with allowance for of reduction conversions Pt (II, IV) allows to realize directional looking up of methods of preparation of platinum catalysts for redox reactions in hydrogen fuel cells.

Keywords: Single-walled nanotubes; Multi-walled nanotubes; Nanofibers; Amorphous carbon; Pt nanoclusters; Fuel cell.

1. Introduction

Pt superfine clusters on conductive supports are effective catalysts of redox reactions proceeding in fuel cells. High specific surface, support conductivity, high dispersity (nanosizes of Pt clusters) and their strong fixation on a surface are necessary criterions of preparation of the effective catalyst. From these points of view CNM for example single- (SWNT) and multi-walled (MWNT) nanotubes, nanofibers (CNF) and x-ray amorphous carbon (AC) can be a successful supports of Pt clusters.

2. Experimental

SWNT were produced by arc-discharge method in the presence of Ni-Y system as catalyst according to [1] at He pressure of 500 Torr. MWNT were synthesized by arc-discharge evaporation of graphite rod with diameter 10 mm at He pressure of 500 Torr and current intensity of 130 A [2] as cathode deposited material. AC was produced by arc-discharge evaporation of graphite rod with diameter 10 mm at He pressure of 500 Torr and current intensity of 100 A [3] as wall deposited soot after exhaustive extraction of fullerenes by toluene. CNF were prepared by pyrolysis of $C_2H_4 - H_2$ mixture (1:1.75 vol.) diluted by Ar (18 % vol.) over $LaNi_5$ at 700°C [4].

CNM oxidation for “anchor” groups introducing was carried out for SWNT by heating (70°C) in concentrated HNO_3 during 24 h, for MWNT – by ultrasonicing of samples in concentrated $HNO_3 - H_2SO_4$ (1:1 v/v) mixture at 40°C for 4 h, for CNF – by heating (70°C) in concentrated HNO_3 during 72 h.

CNM were characterized by chemical analysis, transmission electron microscopy (TEM) with use of electronic microscope EMV-100B and x-ray diffraction analysis on DRON-1 device. The specific surface was measured by

BET method on N_2 used Quantachrome device of Quantasorb company (USA). The thermogravimetric measurements were carried out on the Q-1500 D apparatus at forced air feed of $10 \text{ cm}^3 \cdot \text{min}^{-1}$, soot mass of 10 mg and increasing rate of temperature of $10^\circ\text{C} \cdot \text{min}^{-1}$ in a quartz flask of particular construction.

3. Results and Discussion

Crude CNM inclusive carbon fragments without function groups are hydrophobic and as graphite does not form a compounds with Pt ions. The specific surface is $380 \text{ m}^2 \cdot \text{g}^{-1}$ for SWNT and $290 \text{ m}^2 \cdot \text{g}^{-1}$ for AC. The carbon atoms in these fragments are bound with each other by different types of bonds. SWNT after purification as ideal are arranged as weldless hollow cylinder with external diameter about 1.4-1.6 nm (Fig. 1, a). The cylinder wall consist of convolute graphene letters with aromatic carbon – carbon bonds. These bonds in contrast to common aromatic bonds for example in benzene not undergo to electrophilic substitution and are reactionless. In the pattern of MWNT intercalary one in other hollow cylinders with external diameter about 20-30 nm from convolute graphene letters (Fig. 1, b) or iteratively convolute graphene letter with spherical caps inclusive alternated single and non-conjugated double bonds on nanotube ends are presented. The concentration alternated single and non-conjugated double bonds in comparison with graphene aromatic bonds is very small and these fragments are not presented on figure 1, b.

In the pattern of CNF parallel graphene planars sticks with external diameter about 30-40 nm are presented (Fig. 1, c).

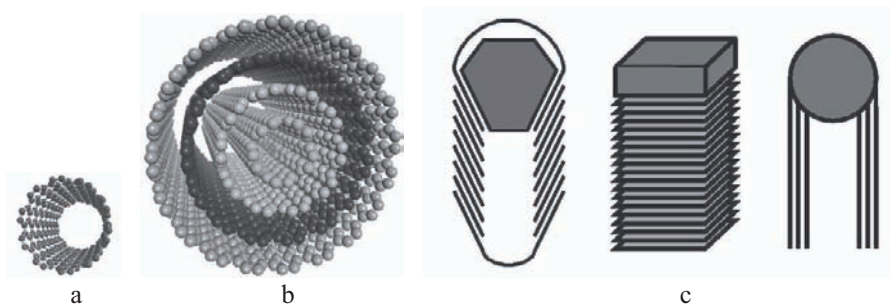


Figure 1. Simplified schemes of SWNT (a), MWNT (b) and different types of CNF (c).

In AC single and non-conjugated double bonds are alternated. These discrepancies in CNM pattern are shown on reactivity in air thermogravimetry (Fig. 2).

For strong Pt fixation on CNM surface it is necessary to introduce functional groups, preferable from ones are $-\text{COOH}$, $-\text{OH}$ and quinoid. The diversity of carbon allotropic forms and types of bonds between carbon atoms causes the different approaches to inculcation of a functional groups on CNM surface.

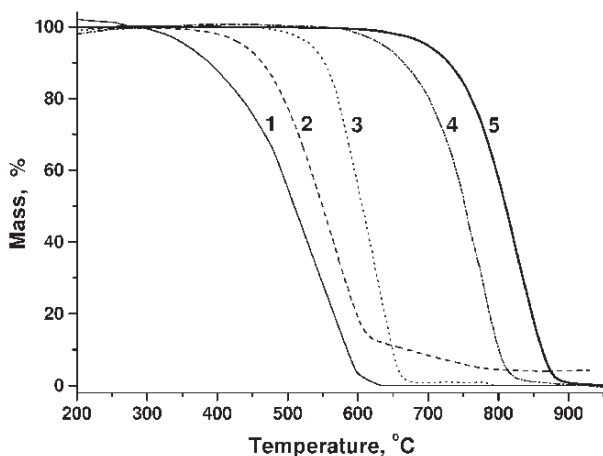


Figure 2. TG curves for carbon nanomaterials: 1 – AC, 2 – SWNT, 3 – CNF, 4 – MWNT, 5 – graphite.

In particular, into SWNT and MWNT, which ones represent the convolute graphene planars, function groups, as well as in case of graphite, are possible to introduce by treatment by strong oxidants such as concentrated HNO_3 or HNO_3 - H_2SO_4 mixture. CNF are more reactive, though at their pattern also are presented by graphene planar stacks. The “anchor” groups to this materials are introduced by HCl and diluted HNO_3 treatment. One oxygen atom per 22 carbon atoms can be introduced into CNF by mixture HNO_3 - H_2SO_4 oxidation, in comparison with SWNT - 1 O atom per 37 C atoms and with MWNT - 1 O atom per 97 C atoms.

More wide opportunities for Pt fixation are available in the case of AC. The H_2PtCl_6 treatment of AC enables Pt addition to double bond without initial material pretreatment. Bromination [3] and the alkaline hydrolysis allow to enter one such group per 7-8 C atoms.

The functional groups introducing into SWNT, MWNT and CNF destroys their aromatic bonds and decreases their conductivity therefore MWNT, wherein conductivity is ensured interior not affected by treatment layers, is suitable support. Really, at total concentration one O atom per 97 C atoms, on a surface more than 1 O atom per 25 C atoms is present.

After functional “anchor” groups introduction on a CNM surface the platinum can be applied from PtCl_4^{2-} or PtCl_6^{2-} ions solutions. $\text{Pt}(\text{NO}_2)_4^{2-}$, $\text{Pt}(\text{OH})_6^{2-}$ ions and other Pt compounds formed with these groups tenuous bridging -O-O- and only donor-acceptor bonds for this purpose are unsuitable. At interaction PtCl_4^{2-} or PtCl_6^{2-} with -OH or -COOH groups HCl is yielded, therefore introducing in a reaction mixture of base, which is not generates $\text{Pt}(\text{OH})_6^{2-}$, is necessary. This opinion is the main difference of our approach against papers devoted to this [5, 6].

For transformation into the active form CNM with supported Pt (II, IV) the reductions up to Pt(0) require. For this purpose not all reducing agents are applicable. In particular, as a result of reduction Pt (IV) supported on SWNT, MWNT or CNF by HCOO^- ion at Pt content 12 % mass. we obtain Pt (0) clusters dimensioned 10-20 nm (Figs. 3-5).

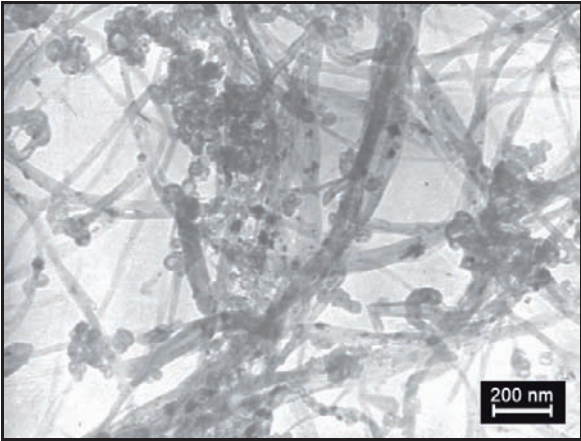


Figure 3. TEM image of 12 % Pt/SWNT.



Figure 4. TEM image of 12 % Pt/MWNT.

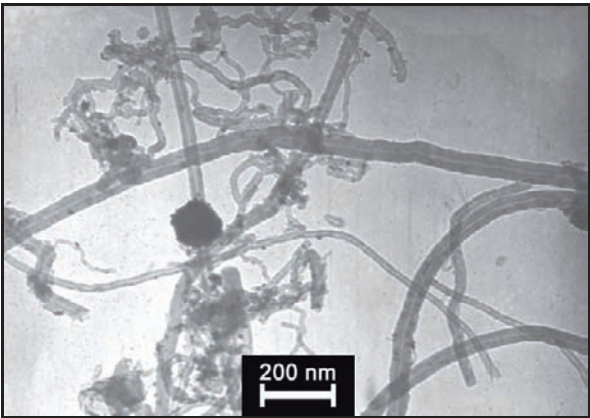


Figure 5. TEM image of 12 % Pt/CNF.

X-Ray diffraction pattern show that Pt(0) clusters average size on Sherrer equation is 7 - 10 nm. For Pt/SWNT clusters size is ~ 4 nm (Fig. 6). It is necessary to mark that the sizes of Pt clusters of traditional catalysts 10 % Pt/C are more (100-200 nm).

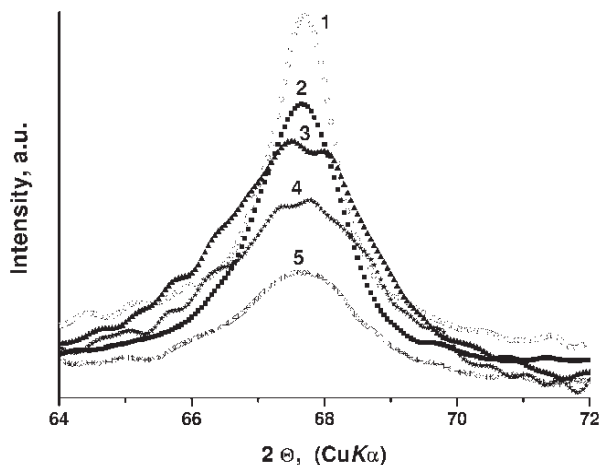


Figure 6. x-Ray diffraction pattern of Pt-supported catalysts (12 % wt. Pt): 1 – Pt/AC, 2 – Pt/CNF, 3 – Pt/MWNT, 4 – Pt/AC-OH, 5 – Pt/SWNT.

Hydrogen reduction of Pt (II, IV)/CNM yields a pyrophoric forms, which are unsuitable for use in fuel cells. These materials reduction by BH_4^- , $\text{N}_2\text{H}_6^{2+}$, NH_2OH or its salts generate boride or nitride forms required hydrogen activation and, as stated above, are unsuitable for use in fuel cells.

Acknowledgment

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THE CONFIGURATIONAL HEAT CAPACITY OF FULLERITE OVER THE REGION OF SCL $\leftrightarrow$ FCCL PHASE TRANSITION

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Abstract. The statistical calculation of the temperature dependence of heat capacity of ordering two-component fullerite has been fulfilled in the approximation of pair interaction between fullerenes by the method of average energies in the model of spherically symmetrical stiff balls.

Keywords: fullerite, heat capacity, order parameter, phase transition.

1. Introduction

Experimental investigation of the temperature dependence of heat capacity of solid-phase fullerite showed the availability of abrupt peak of capacity in the region of temperature $T_0 = 249\text{--}260$ K [1-5] (Fig. 1).

Below the T_0 temperature fullerite has simple cubic lattice (*sc*), above this temperature it has face-centered cubic lattice (*fcc*) and in the area of T_0 temperature the first-kind phase transition from *sc* phase to *fcc* phase occurs. The orientation ordering takes place in fullerite that was experimentally studied in papers [6-11] and at ~ 260 K the *fcc* lattice was formed from the simple cubic one due to this orientation ordering. The orientation ordering is defined not only by temperature, but by pressure as well [12].

Below the statistical-thermodynamical calculation of configurational heat capacity of ordering two-component fullerite from fullerenes $\Phi_1 = C_{60}$, $\Phi_2 = C_{70}$ has been performed and the capacity evaluation has been made over the region of *sc* $\leftrightarrow$ *fcc* phase transition.

The solidphase fullerite of any composition has been produced experimentally [13-17]. It is naturally to assume that Φ_1 , Φ_2 fullerenes behaviour is identical in the solid solution of fullerite. So, it can be proposed that the sites of first and second type, corresponding to the Φ_1 , Φ_2 fullerenes, respectively, can interchange their role during the ordering process. Figure 2 illustrates such superstructures of fullerite with *sc* and *fcc* lattices of B1 structure (NaCl type) and L1₀ structure (CuAu type), respectively.

2. Theory

For solving the posed problem the free energies of *sc* and *fcc* phases are calculated by the method of average energies in the model of spherically symmetrical stiff balls [18]. Calculation of free energies f_1 , f_2 for one site (fullerene) of crystal lattice gives the following formulae

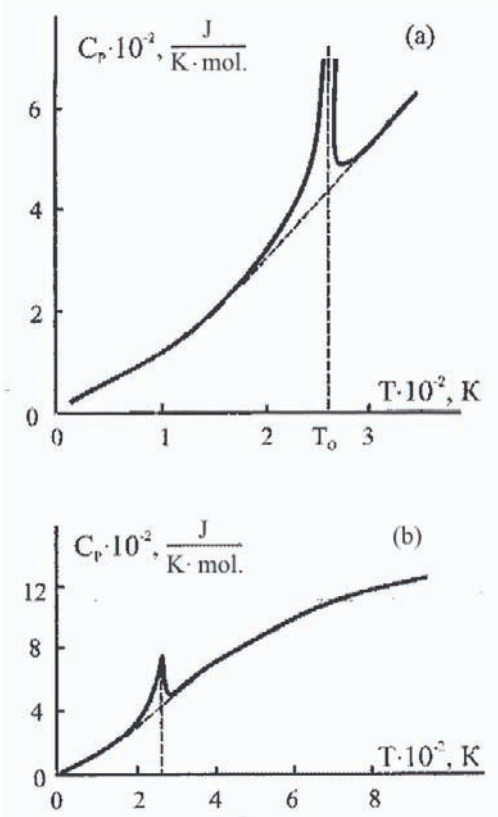


Figure 1. Experimental plots of the temperature dependence of heat capacity for fullerite according to [2] (a) and [8] (b). T_0 is the temperature of $sc1 \leftrightarrow fcc1$ structure phase transition.

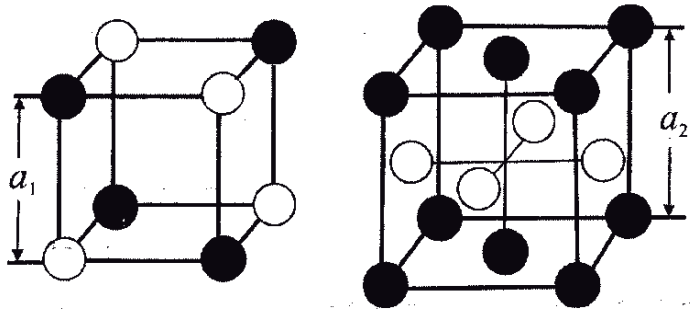


Figure 2. The elementary cells of the fullerite crystal lattice of sc phase (a) of B1 structure (NaCl type) and fcc phase (b) of $L1_0$ structure (CuAu type).

- - lattice sites of the first type corresponding to $\Phi_1 = C_{60}$ fullerenes,
- - lattice sites of the second type corresponding to $\Phi_2 = C_{70}$ fullerenes.

$$f_1 = e_1 - \frac{3}{4} \omega_1 \eta_1^2 + \frac{1}{2} kT \Delta_1 \quad \text{for } sc \text{ phase, [19]} \quad (1)$$

$$f_2 = e_2 - \frac{1}{2} \omega_2 \eta_2^2 + \frac{1}{2} kT \Delta_2 \quad \text{for } fcc \text{ phase, [20]} \quad (2)$$

where e_1 , e_2 terms are defined by energies of interaction between $\Phi_i \Phi_j$ ($i, j = 1, 2$) fullerene pairs and by fullerite composition (the c_1 , c_2 concentrations of Φ_1 , Φ_2 fullerenes with $c_1 + c_2 = 1$) and do not depend on the η_1 , η_2 order parameters in *sc* and *fcc* phases, respectively, ω_1 , ω_2 are the ordering energies of phases, k is Boltzmann's constant, T is absolute temperature and

$$\begin{aligned} \Delta_i = & (c_1 + \frac{1}{2} \eta_i) \ln(c_1 + \frac{1}{2} \eta_i) + (c_1 - \frac{1}{2} \eta_i) \ln(c_1 - \frac{1}{2} \eta_i) + \\ & + (c_2 - \frac{1}{2} \eta_i) \ln(c_2 - \frac{1}{2} \eta_i) + (c_2 + \frac{1}{2} \eta_i) \ln(c_2 + \frac{1}{2} \eta_i), \quad i = 1; 2. \end{aligned} \quad (3)$$

It should be pointed out that the η_i order parameter in formula (3) is equal to η_1 or η_2 for *sc* and *fcc* phases, respectively.

The first two terms of formulae (1), (2)

$$\varepsilon_1 = e_1 - \frac{3}{4} \omega_1 \eta_1^2, \quad (4)$$

$$\varepsilon_2 = e_2 - \frac{1}{2} \omega_2 \eta_2^2 \quad (5)$$

define the internal configurational energies of phases, by which the heat capacities can be determined as follows

$$C = \frac{\partial \varepsilon_1}{\partial T} = -\frac{3}{2} \omega_1 \eta_1 \frac{d\eta_1}{dT} \quad \text{for } sc \text{ phase,} \quad (6)$$

$$C = \frac{\partial \varepsilon_2}{\partial T} = -\omega_2 \eta_2 \frac{d\eta_2}{dT} \quad \text{for } fcc \text{ phase.} \quad (7)$$

The η_1 , η_2 order parameters and their derivatives $\partial \eta_1 / \partial T$, $\partial \eta_2 / \partial T$ should be determined from the conditions of equilibrium state of system, i.e. from equality

$$\partial f_1 / \partial \eta_1 = 0, \quad \partial f_2 / \partial \eta_2 = 0. \quad (8)$$

Substituting the free energies (1), (2) into (8), we find relations

$$kT \ln \frac{(c_1 + \frac{1}{2} \eta_1)(c_2 + \frac{1}{2} \eta_1)}{(c_1 - \frac{1}{2} \eta_1)(c_2 - \frac{1}{2} \eta_1)} = 6\omega_1 \eta_1, \quad (9)$$

$$kT \ln \frac{(c_1 + \frac{1}{2} \eta_2)(c_2 + \frac{1}{2} \eta_2)}{(c_1 - \frac{1}{2} \eta_2)(c_2 - \frac{1}{2} \eta_2)} = 4\omega_2 \eta_2, \quad (10)$$

which define the dependence of order parameters on temperature and fullerite composition $\eta_1 = \eta_1(T, c_1)$, $\eta_2 = \eta_2(T, c_2)$.

Differentiating the equations (9), (10) with respect to temperature, we estimate the derivatives

$$\frac{d\eta_1}{dT} = k \ln \frac{(c_1 + \frac{1}{2}\eta_1)(c_2 + \frac{1}{2}\eta_1)}{(c_1 - \frac{1}{2}\eta_1)(c_2 - \frac{1}{2}\eta_1)} \bigg/ [6\omega_1 - kT \frac{c_1 c_2 - \frac{1}{4}\eta_1^2}{(c_1^2 - \frac{1}{4}\eta_1^2)(c_2^2 - \frac{1}{4}\eta_1^2)}], \quad (11)$$

$$\frac{d\eta_2}{dT} = k \ln \frac{(c_1 + \frac{1}{2}\eta_2)(c_2 + \frac{1}{2}\eta_2)}{(c_1 - \frac{1}{2}\eta_2)(c_2 - \frac{1}{2}\eta_2)} \bigg/ [4\omega_1 - kT \frac{c_1 c_2 - \frac{1}{4}\eta_2^2}{(c_1^2 - \frac{1}{4}\eta_2^2)(c_2^2 - \frac{1}{4}\eta_2^2)}]. \quad (12)$$

Assuming in (9), (10) $\eta_1 \rightarrow 0$, $\eta_2 \rightarrow 0$, we find the ordering temperatures of *sc* and *fcc* phases as follows

$$kT_1 = 6\omega_1 c_1 c_2, \quad (13)$$

$$kT_2 = 4\omega_2 c_1 c_2. \quad (14)$$

After substitution of the derived derivatives (11), (12) into formulae (6), (7) with regard to formulae (13), (14), we get the heat capacity $C_i = C_1$ or C_2 as follows

$$\frac{C_i}{k} = \frac{1}{4}\eta_i \ln \frac{(c_1 + \frac{1}{2}\eta_i)(c_2 + \frac{1}{2}\eta_i)}{(c_1 - \frac{1}{2}\eta_i)(c_2 - \frac{1}{2}\eta_i)} \bigg/ \left[\frac{T}{T_i} c_1 c_2 \frac{c_1 c_2 - \frac{1}{4}\eta_i^2}{(c_1^2 - \frac{1}{4}\eta_i^2)(c_2^2 - \frac{1}{4}\eta_i^2)} - 1 \right], \quad i = 1; 2. \quad (15)$$

This formula (15) defines dependence of configurational heat capacity of *sc* phase at $i = 1$ and *fcc* phase at $i = 2$, respectively, on temperature and c_1 , c_2 concentrations of fullerite.

For fullerite of stoichiometric composition ($c_1, c_2 = 0,5$) the formulae (15) are simplified and take the form

$$\frac{C_i}{k} = \frac{1}{2}\eta_i \ln \frac{1 + \eta_i}{1 - \eta_i} \bigg/ \left(\frac{T}{T_i} \frac{1}{1 - \eta_i^2} - 1 \right), \quad i = 1; 2. \quad (16)$$

In this case the calculation of the ordering temperatures gives the following formulae

$$kT_1 = \frac{3}{2}\omega_1, \quad kT_2 = \omega_2, \quad (17)$$

and the equations (9), (10) of equilibrium states of phases can be written, in view of the ordering temperatures (17), as the relation

$$\frac{T}{T_i} \ln \frac{1 + \eta_i}{1 - \eta_i} = 4\eta_i. \quad (18)$$

The derived formulae (16), (18) allow us to elucidate the character of temperature dependence of the configurational heat capacity of *sc* and *fcc* phases of fullerite of stoichiometric composition over the region of temperatures of phase transition from one phase to another.

3. Discussion of theoretical results, comparison with experiment

For elucidation of the temperature dependence of the configurational heat capacity of fullerite of stoichiometric composition the theory proposes that phase transition occurs in ordered phases, when $\eta_1 \neq 0$ and $\eta_2 \neq 0$. So, it can be assumed that the T_0

temperature ($kT_0=0,022$ eV) of the $scl \leftrightarrow fccl$ phase transition is below the ordering temperatures T_1 , T_2 of these phases. In this case it is possible that the ordering temperature of one phase can be both above and below the ordering temperature of another phase, i.e.

$$T_0 < T_1, T_2, \quad 1) T_1 > T_2, \quad 2) T_1 < T_2. \quad (19)$$

We consider the both cases.

The T_0 temperature of studied $scl \leftrightarrow fccl$ phase transition can be defined from equality of free energies (1), (2) and the calculation gives the following result

$$kT_0 = [2(e_2 - e_1) + \frac{1}{2}(3\omega_1\eta_1^2 - 2\omega_2\eta_2^2)]/(\Delta_1 - \Delta_2), \quad (20)$$

where the $\Delta_i = \Delta_1$, Δ_2 values for fullerite of stoichiometric composition are determined by formula

$$\Delta_i(\eta_i) = (1 + \eta_i) \ln \frac{1 + \eta_i}{2} + (1 - \eta_i) \ln \frac{1 - \eta_i}{2}. \quad (21)$$

The equation (20), inequalities (19), formula (18) and the experimental values of the T_0 temperature of phase transition ($T_0=249-260$ K, $kT_0=0,022$ eV) permit us to evaluate the energetic parameters of system.

As an example we select the T_0 , T_1 , T_2 temperatures according to (19), the ω_1 , ω_2 ordering energies according to (17), the e_2-e_1 energetic parameters according to (20) and the following order parameters at $T = T_0$

$$1) \begin{cases} kT_0 = 0,022 \text{ eV}, & e_2 - e_1 = -0,007 \text{ eV}, \\ kT_1 = 0,0285 \text{ eV}, & \omega_1 = 0,019 \text{ eV}, \quad \eta_1 = 0,73, \\ kT_2 = 0,026 \text{ eV}, & \omega_2 = 0,026 \text{ eV}, \quad \eta_2 = 0,6, \end{cases} \quad (22)$$

$$2) \begin{cases} kT_0 = 0,022 \text{ eV}, & e_2 - e_1 = -0,0003 \text{ eV}, \\ kT_1 = 0,024 \text{ eV}, & \omega_1 = 0,016 \text{ eV}, \quad \eta_1 = 0,4, \\ kT_2 = 0,026 \text{ eV}, & \omega_2 = 0,026 \text{ eV}, \quad \eta_2 = 0,6. \end{cases} \quad (23)$$

According to the chosen values of ordering temperatures $T_i=T_1$, T_2 and numerical values of order parameters for all temperatures, we ascertain the temperature dependence of order parameter in phases, defined by formula (18). Figure 3 demonstrates the curve plots of dependences $\eta_1(T)$, $\eta_2(T)$ for $T_1 > T_2$ (curve 1 at $kT = 0,0285$ eV) and $T_1 < T_2$ (curve 2 at $kT = 0,024$ eV) for the ordering temperature of fcc phase equal to $kT = 0,026$ eV and for the temperature of $scl \leftrightarrow fccl$ phase transition equal to $kT_0 = 0,022$ eV. This plots make it possible to estimate the values of the η_1 , η_2 order parameters at the T_0 temperature of phase transition and they are equal to $\eta_1 = 0,73$; $0,4$ and $\eta_2 = 0,6$, as in (22), (23). These values of η_1 , η_2 parameters are used for determination of the e_2-e_1 energetic constants in (22), (23) by formulae (20), (21). For this purpose the dependence $\Delta_i(\eta_i)$ is plotted and the Δ_i values have been calculated for order parameters $\eta_1 = 0,4$; $0,73$; $\eta_2 = 0,6$. These values are equal to

$$\begin{aligned} 1) \Delta_1 &= -1,22 \quad \text{at} \quad \eta_1 = 0,4, \\ 2) \Delta_1 &= -0,8 \quad \text{at} \quad \eta_1 = 0,73, \\ \Delta_2 &= -1 \quad \text{at} \quad \eta_2 = 0,6. \end{aligned} \quad (24)$$

Now by the use of the selected values of the $T_i = T_1, T_2$ ordering temperatures (22), (23) and with the determination of numerical values of order parameters for all temperatures by the curve plots of Fig. 3, the temperature dependence of configurational heat capacity can be elucidated by formula (16) and the peculiarities of this dependence can be established over the region of $sc \leftrightarrow fcc$ phase transition.

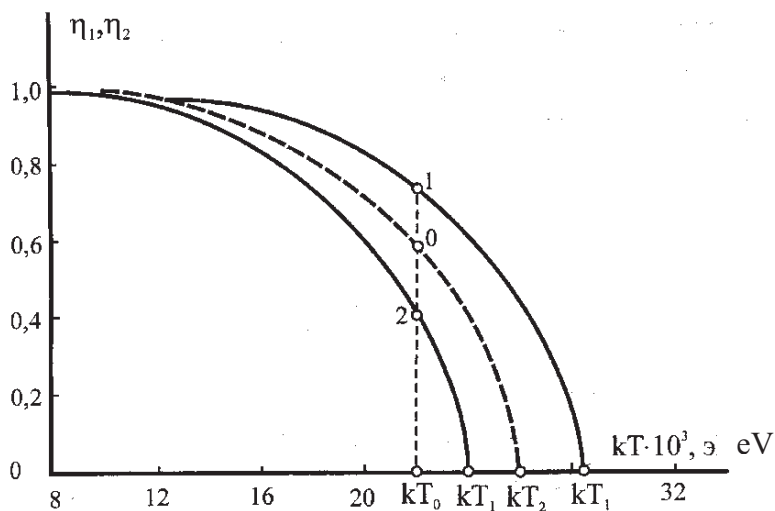


Figure 3. The curve plots of the temperature dependence of order parameters of fullerite of stoichiometric composition for sc (full curves η_1) and fcc (dotted curve η_2) phases. The order parameters η_1 (point 1 for $kT_1 = 0,0285$ eV, point 2 for $kT_1 = 0,024$ eV) and η_2 (point 0 for $kT_2 = 0,026$ eV) at the phase transition temperature kT_0 and also the temperatures kT_0, kT_1, kT_2 on the abscissas axis are marked with circles.

The curve plots of the $C(T)$ dependence are presented in Fig. 4. As evident from Fig. 4, the heat capacity increases with a rise in temperature and undergoes the discontinuous change at the temperatures of the $sc \leftrightarrow fcc$ phase transition and at the temperature of phase transition of order-disorder type in fcc phase. In the first case, when $T_1 > T_2$ (Fig. 4a), the heat capacity increases abruptly at the T_0 temperature and in the second case, when $T_1 < T_2$ (Fig. 4b) decreases. After the step in the point $T = T_0$ the growth of temperature increases the heat capacity again. Further at the ordering temperature $T = T_2$ of fcc phase the heat capacity decreases sharply from the maximum value $C/k = 1,6$ up to value $C/k = 1$. The last value is determined by the formula (16) according to the Lapital rule. At further increase of temperature, when $T_1 > T_2$, the configurational heat capacity is equal to zero. The comparison of Fig. 1 and Fig. 4, corresponding to experimental and calculation data, points to their qualitative agreement.

It should be noted that experimental measurements of heat capacity at $T > T_2$, as a rule, give the values decreased in a gradual manner up to zero (Fig. 1), but not nonzero heat capacity, that is caused by the existence of short-range order in crystal or by correlation in substitution of lattice sites by Φ_1, Φ_2 components, but this is not taken into consideration in the present paper.

Notice also that both of steps of the heat capacity at the T_0 and T_2 temperatures, revealed in calculations, was not found experimentally. In the cited papers the mention is made only of the fact of abrupt increase of heat capacity, but the further careful experimental study is of scientific interest, because such experiments will confirm the presence of the Φ_1 , Φ_2 fullerenes ordering and permit to make an estimate of ordering temperature.

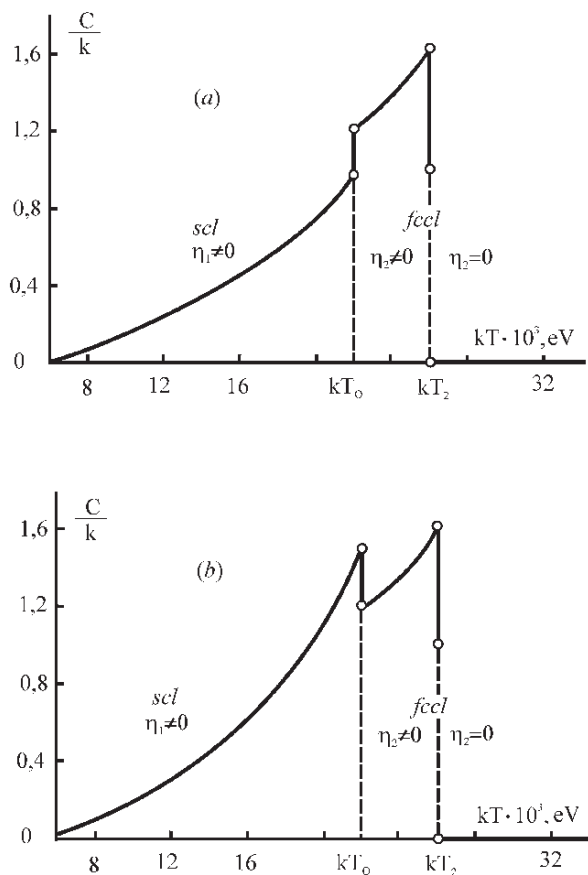


Figure 4. The curve plots of the temperature dependence of configurational heat capacity of fullerite of stoichiometric composition constructed by formulae (16), (18) in the neighbourhood of *scl* $\leftrightarrow$ *fcc* phase transition.

a) $kT_1 > kT_2$, when $\eta_1 > \eta_2$,

b) $kT_1 < kT_2$, when $\eta_1 < \eta_2$.

The steps in heat capacity at temperature kT_0 of the *scl* $\leftrightarrow$ *fcc* phase transition and at temperature kT_2 of order-disorder phase transition in *fcc* phase are marked with circles.

4. Conclusions

The elaborated statistical-thermodynamical calculation makes it possible to elucidate the character of temperature dependence of configurational heat capacity

of *scl* and *fccl* phases of fullerite and to reveal the possible peculiarities of this dependence over the temperature T_0 area of phase transition of fullerite from *scl* to *fccl* phase. The consideration of fullerenes C_{60} , C_{70} ordering determines the possibility of manifestation of two steps on the plots of temperature dependence of heat capacity. As this takes place, the abrupt change of capacity in the point $T=T_0$ can both increase and decrease the capacity value in dependence on the relationship between ordering temperatures in *scl* and *fccl* phases, at the disordering of fullerite the configurational heat capacity goes to zero. The obtained results of theory are in satisfactory agreement with experimental data.

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COMMENTS CONCERNING PARAMETERS OF THE SHORT-RANGE ORDER EVOLUTION DETERMINED FROM THE DATA ON KINETICS OF A HEAT-CAPACITY RELAXATION FOR Lu–H ALLOY

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Abstract. One more method of study of the short-range order kinetics of H-atoms over tetrahedral interstices in lutetium (Lu) is proposed. It can be realized by the using of available data of measurements of heat capacity for h.c.p.-Lu–H interstitial solid solutions during the isothermal annealing. Comparison of estimated-parameters data from heat capacity and residual electrical-resistivity measurements is performed. It is shown that kinetics of heat capacity and residual resistivity at low temperatures is caused by the unique ‘nature’ (short-range order relaxation) and can be described by two relaxation times at least.

Keywords: short-range order, relaxation time, heat capacity, residual electrical resistivity

1. Introduction

Short-range order is the unique natural-occurring concentration heterogeneity, whose sizes are commensurate with lattice parameters of a solid solution. Kinetics of short-range order is determined by the microscopic diffusion over intersite distances. Therefore, kinetic measurements of its relaxation provide us with detailed information on the discrete diffusion mechanism such as the microscopic characteristics of atomic migrations, including probabilities and types of atomic jumps, and diffusion activation energy. The relaxation of radiation diffuse-scattering intensities is a most convenient technique for the investigation of short-range order kinetics [1–3]. Another one is to study the change of physical properties affected by the short-range order evolution, for instance, residual electrical resistivity or heat capacity relaxation, which enables obtaining the results with more simplicity and responsiveness.

This work is concerned with a further analysis of the short-range order kinetics of hydrogen (H) atoms at tetrahedral interstices in h.c.p. lattice of lutetium (Lu). We compare the results obtained from independent investigation methods for different characteristics—residual electrical resistance [4, 5] and heat capacity [6], and reveal the same ‘nature’ of their conditionality.

2. Kinetics models

Because of the macroscopic character of the heat capacity, our model is phenomenological and macroscopic. It is based on the hypothesis that, for any

interstitial mechanism of hydrogen diffusion in h.c.p.-LuH_c ($0 \leq c < 0.5$) solid solution, the reciprocal relaxation time for the i -th type channel of relaxation process, $1/\tau_i$, is directly proportional to the jump frequency (mobility) of H atoms, v_{Hi} , with an efficiency factor χ_i :

$$1/\tau_i = \chi_i(1 - c)v_{Hi}.$$

As assumed, the relaxation time corresponds to the time required for the i -type channel migration of hydrogen to change the short-range order parameter value in e times. The temperature dependence of v_{Hi} has its usual definition given by a Boltzmann distribution:

$$v_{Hi} = v_{0i} \exp[-E_{mi}/(k_B T)].$$

In the last expression, v_{0i} is a pre-exponential factor, k_B —Boltzmann constant, T —annealing temperature, E_{mi} is the migration energy of H atoms over the i -th ‘scenario’. It corresponds to their activation energy, E_{ai} , in a case of spatial redistribution of H atoms between the (tetrahedral) interstices ($E_a \approx E_{mi}$). Therefore, the temperature dependence of τ_i follows the so-called Arrhenius ‘law’:

$$\tau_i = \tau_{0i} \exp[-E_{mi}/(k_B T)], \text{ where } \tau_{0i} = 1/[\chi_i(1 - c)v_{0i}].$$

In this case, experimental data have to be described with only two parameters, τ_{0i} and E_{mi} , for each (i -th) contribution to the relaxation mechanism.

Under stationary conditions, *i.e.* constant concentration of H atoms as interstitial defects, the relaxation of a heat capacity for the Lu–H can be described within the frameworks of the first-order kinetics model,

$$\Delta C_p(t, T)/\Delta C_{p0}(T) \approx e^{-t/\tau}, \quad dC_p(t, T)/dt \approx -\Delta C_p(t, T)/\tau,$$

or with more realistic second-order kinetics model,

$$\begin{aligned} \Delta C_p(t, T)/\Delta C_{p0}(T) &\approx A e^{-t/\tau_1} + (1 - A) e^{-t/\tau_2}, \\ dC_p(t, T)/dt &\approx -\Delta C_{p0}(T) \{A [e^{-t/\tau_1}]/\tau_1 + (1 - A) [e^{-t/\tau_2}]/\tau_2\}; \end{aligned}$$

$\Delta C_p(t, T) = C_p(t, T) - C_{p\infty}(T)$, $\Delta C_{p0}(T) = C_{p0}(T) - C_{p\infty}(T)$, $C_p(t, T)$ is instantaneous heat capacity (at the t point of time), $C_{p0}(T)$ is initial ($t = 0$) heat capacity, and $C_{p\infty}(T)$ is ‘equilibrium’ ($t \rightarrow \infty$) heat capacity at annealing temperature T ; A and $(1 - A)$ are ‘weights’ of the first relaxation ‘scenario’ and of the second one, respectively.

So, determining the relaxation times of heat capacity from its measurements during the isothermal ($T = \text{const}$) annealing of Lu–H, we obtain relaxation time, τ_i , which is connected with the jump frequency of H atoms, v_{Hi} . Values of τ_i are the short-range order relaxation times of H in Lu.

3. Results

Kinetics of heat-capacity (C_p) relaxation was experimentally studied in Ref. [6] for h.c.p.-Lu–H single crystal. Changes of $dC_p(t, T)/dt$ vs. time t for LuH_{0.148} during the isothermal annealing were observed at temperatures from 130 K to 180 K [6]. Experimental results of heat-capacity measurements for LuH_{0.148} are represented

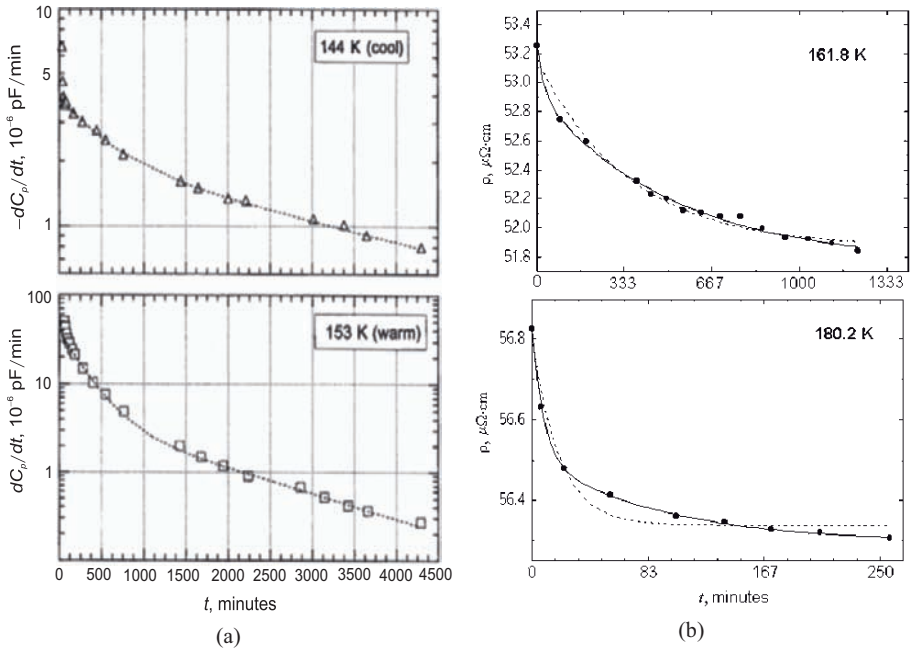


Figure 1. Heat-capacity derivative, dC_p/dt , [6] and residual-resistivity, ρ , [8] dependences on time for LuH_{0.148} (a) and LuH_{0.180} (b) solid solutions at different annealing temperatures. In Fig. 1(b), ●—experimental data from Ref. [5], dash curve corresponds to the first-order kinetics model, and solid curve represents the second-order kinetics model.

in Figs. 1(a). These results can be described within the framework of both above-mentioned first- and second-order kinetics models, but in order to keep analysis trustworthy, author of [6] used the second-order kinetics model with two relaxation times (see Fig. 2(a)). Using the Arrhenius ‘law’, migration energies of H atoms in LuH_{0.148} were estimated and listed in Table 1.

Changing a heat capacity, C_p , in above-mentioned equations into the residual electrical resistivity, ρ , they can be reduced to the corresponding kinetics models as applied to describe the results of residual resistivity measurements [5] for LuH_{0.180} and LuH_{0.254}. Experimental [5] and theoretical [7], [8] results of investigation of the short-range order relaxation in LuH_{0.180} and LuH_{0.254} polycrystals were obtained from data about measurements of residual-resistivity–time dependence and are presented in Fig. 1(b). These results we described within the framework of the first- and second-order kinetics models as well (see Fig. 1(b)). Migration energies for LuH_{0.180} and LuH_{0.254} solid solutions were evaluated and are listed in Table 1.

4. Discussions and conclusions

As noted in Ref. [6], two fitting parameters, τ_1 and τ_2 , are chosen for more ‘high-quality’ reproduction of measuring data. Nevertheless, in fact, the sense of these parameters is more intimate. Characterization of both heat-capacity and residual-resistivity relaxation kinetics (following the short-range order evolution kinetics) for

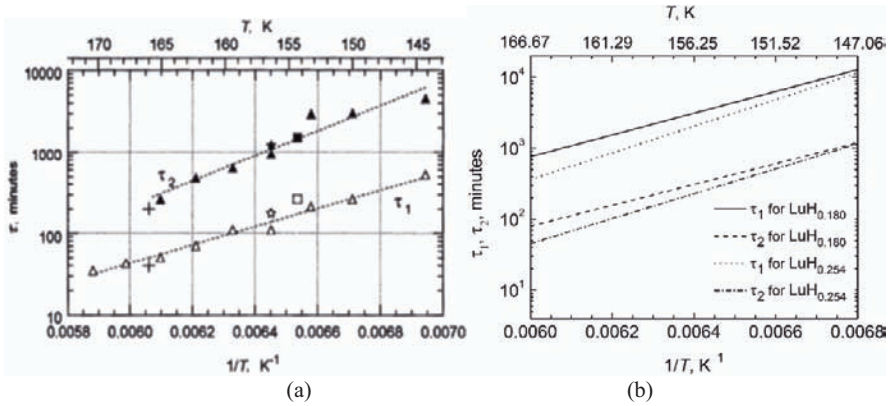


Figure 2. Heat-capacity (a) and residual-resistivity (b) relaxation times, τ_1 and τ_2 , vs. reciprocal annealing temperature, $1/T$, within the framework of the second-order kinetics model for h.c.p.-Lu-H solid solutions; (a)—for $LuH_{0.148}$ [6], (b)—for $LuH_{0.180}$ and $LuH_{0.254}$.

Lu-H on the whole by the two relaxation times may be caused by the difference of probabilities of interstitial H-atoms' jumps along the preferential directions of ' a_0 ' and ' c_0 ' axes in h.c.p. lattice of Lu single crystal or of every crystallite in Lu polycrystal (even in spite of the isotropy of scalar C_p value).

Moreover, in contrast to the author of Ref. [6], it seems to us that 170 K data in Ref. [6] have to be represented by the two time parameters, as well. To be sure of that, 170 K data measurements must be performed over a long period of time (see Fig. 8 in Ref. [6]).

Evidently on average, the presented migration energy for more concentrated $LuH_{0.180}$ solution, $(E_{m1} + E_{m2})/2 = 0.295$ eV (based on ρ data), exceeds reasonably the migration energy for less concentrated $LuH_{0.148}$ solution, $(E_{m1} + E_{m2})/2 = 0.26$ eV (based on C_p data). Such a correlation between the increase of activation energy and the rise of c suggests that the factors determining the relaxation kinetics of two different characteristics— C_p and ρ —are concerned with each other.

Besides, the average of the migration energies for two time constants estimated from the data on heat capacity in Ref. [6] is the same as that determined in the isochronal residual resistivity recovery experiments [9], *i.e.* 0.27 eV. Moreover, relaxation times of residual resistivity for $LuH_{0.180}$ or $LuH_{0.254}$ and heat capacity for $LuH_{0.148}$ are similar to each other for the given low (below 200 K) temperatures (see Fig. 2). These facts once again suggest that, for low temperatures, these two quite different experiments involve the same phenomenon and are conditioned by the same 'nature'—short-range order relaxation.

On another hand, migration energies calculated in Ref. [6] differ significantly from the isothermal residual resistance recovery measurements obtained by authors in Refs. [5] (0.45 eV), [10] (0.43 eV) and from the Gorsky effect determination with self-diffusion of H in Lu [11] (0.575 eV). Why does such a discrepancy exist?

In fact, caused by the short-range order relaxation, the residual-resistivity and heat-capacity relaxation kinetics at low temperatures cannot be represented by a single time constant and sometimes even by two time constants. According to the Khachaturyan's approach [1] (see also [7, 8]), in a general case, the short-range order

kinetics should be described by help of three exponentials, *i.e.* by three relaxation times. If two or all three relaxation times coincide with each other only, it can manifest oneself with two or one relaxation times, respectively. So, to describe C_p and ρ at low temperatures, two relaxation times should be used at least.

It is necessary to note in conclusion that now using available data of time dependence of one characteristic, for example, heat capacity, we can predict the behaviour of another one, for example, electrical resistivity, and vice versa (for predictions of radiation diffuse scattering, see in Ref. [8]).

TABLE 1. Migration energies for Lu–H within the framework of the 1-st and 2-nd order kinetics models

Alloy	1-st order model	2-nd order model	
	E_m , eV	E_{m1} , eV	E_{m2} , eV
Single crystalline LuH _{0.148}		0.22 [6]	0.31 [6]
Polycrystalline LuH _{0.180}	0.33	0.30	0.29
Polycrystalline LuH _{0.254}	0.38	0.37	0.35

Acknowledgement

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TRIFLUOROMETHYLATION OF ENDOHEDRAL METALLOFULLERENES $M@C_{82}$ ($M = Y, Ce$): SYNTHESIS, ISOLATION AND STRUCTURE

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Abstract. Endohedral metallofullerenes were for the first time trifluoromethylated to afford the isolation and characterization of two isomers of $Y@C_{82}(CF_3)_5$ and of three isomers of $Ce@C_{82}(CF_3)_5$. All of the purified new compounds were characterized by S_8 -MALDI mass spectrometry, UV-vis and by 1D and 2D-COSY ^{19}F NMR spectroscopy. The most probable structures proposed from the NMR data and quantum chemical calculations, contain 1,4 chains of CF_3 groups.

Keywords: A. Fullerene; B. Arc discharge, Chemical treatment; C. Chromatography, Nuclear magnetic resonance

1. Introduction

New carbon compounds, namely, endohedral metallofullerenes (EMFs) are promising building blocks to be used in the design of nanosized materials of a new generation. They exhibit unique electrical, magnetic and chemical properties. Now fullerene chemistry is most developed due to that fullerenes are accessible to a wide range of researchers. However, chemical properties of EMFs are very weakly studied because of problems of the synthesis and isolation of pure EMFs in preparative quantities.

The first chemical modification of EMFs, the cycloaddition of disilacyclopropane to $\text{La}@\text{C}_{82}$, was reported in 1995 [1]. Several other groups also reported cycloadducts of EMFs [2,3], but unambiguous structural characterization was achieved only in one study [4]. More recently, water-soluble EMFs, the $\text{Gd}@\text{C}_{60}(\text{C}(\text{COOH})_2)_{10}$ cycloadduct reported by Bolskar et al. [5], have been prepared to explore their potential use as MRI contrast agents [5,6], and Shinohara et al. used fluorous biphasic techniques to prepare $\text{La}@\text{C}_{82}(\text{C}_8\text{F}_{17})_2$ [7]. Until this work, however, $\text{La}@\text{C}_{82}(\text{C}_8\text{F}_{17})_2$ was the only reported exohedral derivative of EMFs with atomic substituents such as H, F, Cl, or Br, or with organic substituents R having only R–C_{EMF} single bonds.

In this work, we for the first time suggested to replace neutral EMFs by their stable anionic complexes, which can be prepared on a gram scale, to prepare trifluoromethyl derivatives and study chemical properties of EMFs $\text{M}@\text{C}_{82}$ (M = Y, Ce).

2. Experimental

EMFs-containing soots were prepared by burning composite graphite electrodes with metallic yttrium or cerium in an arc-discharge reactor. EMFs $\text{Y}_m@\text{C}_{2n}$ or $\text{Ce}_m@\text{C}_{2n}$ were extracted in a two-stage procedure under an atmosphere of argon (refluxing *o*-dichlorobenzene followed by refluxing *N,N*-dimethylformamide (DMF)) [8,9], resulting in an extract enriched in $\text{M}@\text{C}_{82}$ (M = Y, Ce) and small amounts $\text{M}_2@\text{C}_{80}$ (M = Y, Ce) as evidenced by mass spectrometry [8].

2.1. REACTIONS OF DMF EXTRACT EMFs $\text{Y}_m@\text{C}_{2n}$ AND $\text{Ce}_m@\text{C}_{2n}$ WITH AgCF_3COO

In a typical synthetic experiment, $\text{M}@\text{C}_{82}$ -enriched extract (M = Y, Ce) (100 mg) was thoroughly mixed with AgCF_3COO (Aldrich, 500 mg). The reaction mixture was placed in a quartz reactor under dynamic vacuum (10^{-6} Torr) and heated up to 400 °C at 40 °C/min heating rate for 10 h. The IR spectrum of the cooled product mixture showed that no AgCF_3COO remained. Increasing the AgCF_3COO :EMFs extract ratio above 25:1 did not yield products with more than five CF_3 groups per cage.

2.2. ISOLATION $\text{Y}@\text{C}_{82}(\text{CF}_3)_5$ (ISOMERS I AND II)

For the isolation of pure $\text{Y}@\text{C}_{82}(\text{CF}_3)_5$ (isomer I and II) samples, a two-stage chromatographic procedure was developed. Crude $\text{Y}@\text{C}_{82}(\text{CF}_3)_x$ samples were dissolved in toluene, filtered using a 0.45 μm filter to remove insoluble impurities (mainly of inorganic origin). At the first separation stage, Cosmosil Buckyprep (20 mm i.d. $\times$ 250 mm, Nacalai Tesque Inc., 9 mL injections, 18 mL/min flow rate, toluene eluent) was used for the separation of the two major $\text{Y}_m@\text{C}_{80/82}(\text{CF}_3)_n$ -containing fractions **A** (28 min) and **B** (38 min) (*cf.* C_{60} , 8.8 min). At the second stage, Regis Buckyclutcher column (20 mm i.d. $\times$ 250 mm, Regis Chemical Co., 1.2 mL

injections, 12 mL/min flow rate, toluene eluent) was used for the isolation of the pure compounds from fraction **A**: $\text{Y}@\text{C}_{82}(\text{CF}_3)_5$ (isomer **I**, 6.2 min), $\text{Y}@\text{C}_{82}(\text{CF}_3)_3$ (6.8 min), $\text{Y}_2@\text{C}_{80}(\text{CF}_3)_8$ (8 min), $\text{Y}@\text{C}_{82}(\text{CF}_3)$ (9.8 min); and from fraction **B**: $\text{Y}@\text{C}_{82}(\text{CF}_3)_5$ (isomer **II**) (6.8 min).

2.3. ISOLATION $\text{Ce}@\text{C}_{82}(\text{CF}_3)_5$ (ISOMERS I, II AND III)

For the isolation of pure $\text{Ce}@\text{C}_{82}(\text{CF}_3)_5$ (isomers I, II and III) samples, a two-stage chromatographic procedure was developed. Crude $\text{Ce}@\text{C}_{82}(\text{CF}_3)_x$ samples were dissolved in toluene, filtered using a 0.45 μm filter to remove insoluble impurities (mainly of inorganic origin). At the first separation stage, Cosmosil Buckyprep (20 mm i.d. $\times$ 250 mm, Nacalai Tesque Inc., 9 mL injections, 18 mL/min flow rate, toluene eluent) was used for the separation of the four major $\text{Ce}_m@\text{C}_{80/82}(\text{CF}_3)_n$ -containing fractions **A** (28.6 min), **B** (32.8 min), **C** (42.5 min) and **D** (51 min) (*cf.* C_{60} , 8.8 min). At the second stage, Regis Buckyclutcher column (20 mm i.d. $\times$ 250 mm, Regis Chemical Co., 1.2 mL injections, 12 mL/min flow rate, toluene eluent) was used for the isolation of the pure compounds from fraction **A**: $\text{Ce}@\text{C}_{82}(\text{CF}_3)_5$ (isomer **I**) (7.0 min); from fraction **B**: $\text{Ce}@\text{C}_{82}(\text{CF}_3)_5$ (isomer **II**) (7.2 min); from fraction **C**: $\text{Ce}@\text{C}_{82}(\text{CF}_3)_5$ (isomer **III**) (7.6 min); from fraction **D**: $\text{Ce}_2@\text{C}_{80}$ (13.0 min).

2.4. SPECTROSCOPIC CHARACTERIZATION

The mass spectrometry analysis was performed by the matrix assisted laser desorption/ionisation time-of-flight (S_8 -MALDI) technique using a Voyager-DETM PRO BiospectrometryTM Workstation (Applied Biosystems, USA). Nitrogen laser pulses of 337 nm wavelength, 0.5 ns duration, and 3 Hz frequency were used to desorb the species into the gas phase. Negative or positive ions formed were detected in a reflectron mode. Sulfur used as a matrix material was also dissolved in toluene and mixed with the samples solution prior to deposition onto a target. The UV-Vis-NIR spectra of samples were recorded with a "Varian Cary 500 Scan" UV-Vis-NIR - spectrophotometer" in quartz cells of 10 mm path length from 300 to 1100 nm with a resolution of 1 nm. Samples for ^{19}F NMR spectroscopy were benzene- d_6 solutions at room temperature recorded using a Bruker INOVA-400 spectrometer operating at 376.5 MHz (C_6F_6 internal standard, δ -169.9).

3. Results and Discussion

Figure 1 shows the S_8 -MALDI mass spectrum of the crude product of the high-temperature reaction between the $\text{Ce}@\text{C}_{82}$ -enriched EMFs starting material and silver (I) trifluoroacetate (AgCF_3COO). The main reaction product is $\text{Ce}@\text{C}_{82}(\text{CF}_3)_5$. It is interesting that no EMFs derivative with more than five CF_3 groups was formed since similar high-temperature reactions of AgCF_3COO and empty fullerenes afford $\text{C}_{60/70}(\text{CF}_3)_n$ products with n as high as 22 [10,11].

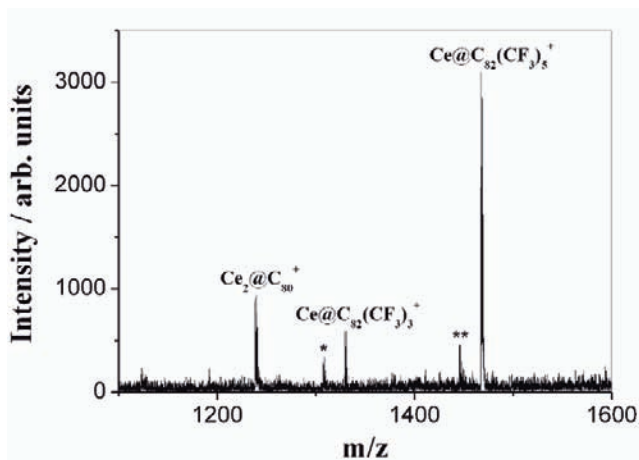


Figure 1. Positive-ion S₈-MALDI mass spectrum of the crude reaction product, Ce@C₈₂(CF₃)_x. Peaks marked with one or two asterisks are assigned to Ce@C₈₀(CF₃)₃⁺ and Ce@C₈₀(CF₃)₅⁺, respectively.

Figure 2 shows the chromatogram of the starting reaction product, Ce@C₈₂(CF₃)_x. Three Ce@C₈₂(CF₃)₅ isomers were isolated from fractions **A**, **B**, **D** and pure Ce₂@C₈₀ was isolated from fraction **D**. In contrast to the reaction of Y-EMFs with silver (I) trifluoroacetate, which affords two Y@C₈₂(CF₃)₅ isomers and Y₂@C₈₀(CF₃)_{1,3} derivatives [12], the reaction with Ce-EMFs affords three Ce@C₈₂(CF₃)₅ isomers and Ce₂@C₈₀ does not react and can be isolated as an individual compound. The HPLC chromatogram and the S₈-MALDI spectrum of isolated Ce@C₈₂(CF₃)₅ (isomer III) are presented in Fig. 3. The mass spectrum shows only the peak with m/z=1469 attributable to Ce@C₈₂(CF₃)₅⁺. The fragmentation of this ion results in the loss of the CF₃ groups up to the formation of the Ce@C₈₂⁺ ion. The 99 % purity of Ce@C₈₂(CF₃)₅ (isomers **I**, **II** and **III**) and Y@C₈₂(CF₃)₅ (isomers **I** and **II**) was determined by HPLC and S₈-MALDI analysis.

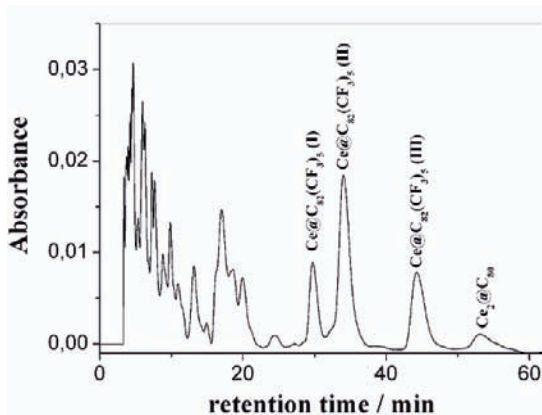


Figure 2. HPLC traces (Cosmosil Buckyrep column) of the crude reaction product, Ce@C₈₂(CF₃)_x.

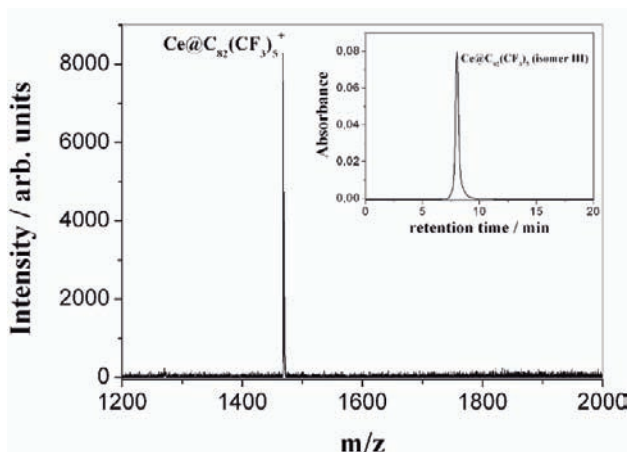


Figure 3. Positive-ion S_8 -MALDI mass spectrum of HPLC-purified $\text{Ce}@C_{82}(\text{CF}_3)_5$ isomer **III**. The inset shows HPLC traces (Buckyclutcher column) of a purified sample of $\text{Ce}@C_{82}(\text{CF}_3)_5$ isomer **III**.

The UV-Vis-NIR spectra of $\text{Ce}@C_{82}(\text{CF}_3)_5$ (isomers **I**, **II** and **III**) dissolved in toluene are shown in Fig. 4. The spectrum of parent $\text{Ce}@C_{82}$ has two characteristic absorption bands at 634 and 1011 nm attributable to the symmetry of the carbon cage, C_{2v} [13]. Isomer **I** $\text{Ce}@C_{82}(\text{CF}_3)_5$ has three characteristic bands at 593, 738 and 987 nm, isomer **II** has four bands at 436, 582, 650 and 872 nm, and isomer **III** has two ones at 593 and 826 nm. The absorption spectra of the isomers are different from that of parent $\text{Ce}@C_{82}$. Seemingly, the formation of exohedral $\text{Ce}@C_{82}(\text{CF}_3)_5$ derivatives is accompanied by strong changes in the band structure of $\text{Ce}@C_{82}$.

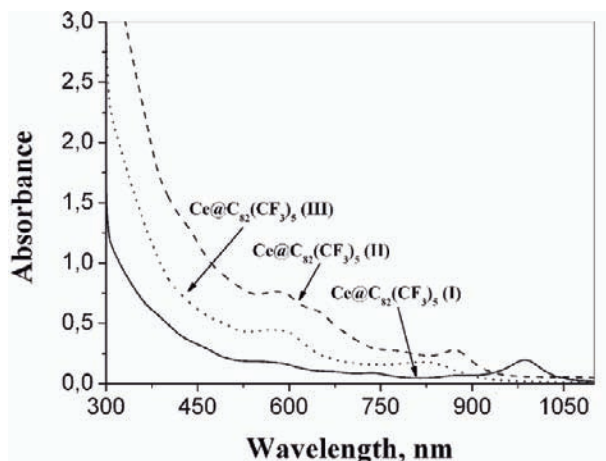


Figure 4. UV-vis-NIR spectrum of HPLC-purified $\text{Ce}@C_{82}(\text{CF}_3)_5$ (isomers **I**, **II** and **III**) and $\text{Ce}@C_{82}$ in toluene.

In contrast to starting EMFs $M@C_{82}$ ($M = Ce, Y$), which are paramagnetic ones, the EMF $M@C_{82}(CF_3)_5$ ($M = Ce, Y$) derivatives are diamagnetic because of the presence of an odd number of substituents that allows their structures to be studied by NMR spectroscopy. Table 1 presents the data on 1D and 2D ^{19}F NMR spectroscopy for all compounds isolated. The ^{19}F ЯMP spectrum of every compound involves five resonance lines. Each line is attributed to the three fluorine atoms of one of the CF_3 groups. The lines have a hyperfine structure due to the splitting of a nuclear spin of the fluorine atom of one CF_3 group on ^{19}F nuclei of the adjacent CF_3 group. Thus, a conclusion can be drawn on that all CF_3 groups of the molecule are not equivalent but located as a chain in the same part of the carbon cage. In our previous work [12], we showed using the DFT data that the most probable topology is the addition of CF_3 groups of 1,4 chains. Fig. 5 shows the Schlegel diagrams of the most stable structures for $Y@C_{82}(CF_3)_5$ [12].

TABLE 1. ^{19}F NMR Data

Compound	Multiplet/ $-\delta$ /res. nos. of COSY correlations				
$C_1-Y@C_{82}(CF_3)_5$ (I)	a	b	c	d	e
$-\delta$	52.8	53.1	63.6	66.9	69.1
m	qq	qq	qq	q	q
COSY	c,e	c,d	a,b	b	a
J_{FF}	12.4	11.3, 13.6	11.3, 13.2	13.8	12.0
$C_1-Y@C_{82}(CF_3)_5$ (II)	a	b	c	d	e
$-\delta$	52.8	52.8	63.5	68.3	69.1
m	m	m	qq	q	q
COSY	d,c	c, e	a,b	a	b
J_{FF}	ca.12.8	ca.12.8	10.9, 13.2	13.6	12.7
$C_1-Ce@C_{82}(CF_3)_5$ (I)	a	b	c	d	e
$-\delta$	62.1	62.1	63.3	67.8	70.9
m	m	m	qq	q	q
COSY	d,c	e,c	a,b	a	b
J_{FF}	-	-	12.0, 13.2	14.3	14.7
$C_1-Ce@C_{82}(CF_3)_5$ (II)	a	b	c	d	e
$-\delta$	54.1	56.7	66.5	70.1	70.6
m	qq	qq	qq	q	q
COSY	c,e	c,d	a,b	b	a
J_{FF}	12.0, 12.8	9.9, 13.6	11.2, 13.2	13.6	11.6
$C_1-Ce@C_{82}(CF_3)_5$ (III)	a	b	c	d	e
$-\delta$	55.6	55.7	67.2	70.8	71.4
m	qq	qq	qq	q	q
COSY	c,d	e,c	a,b	a	b
J_{FF}	ca.12.8	12.8	12.8	13.6	12.8

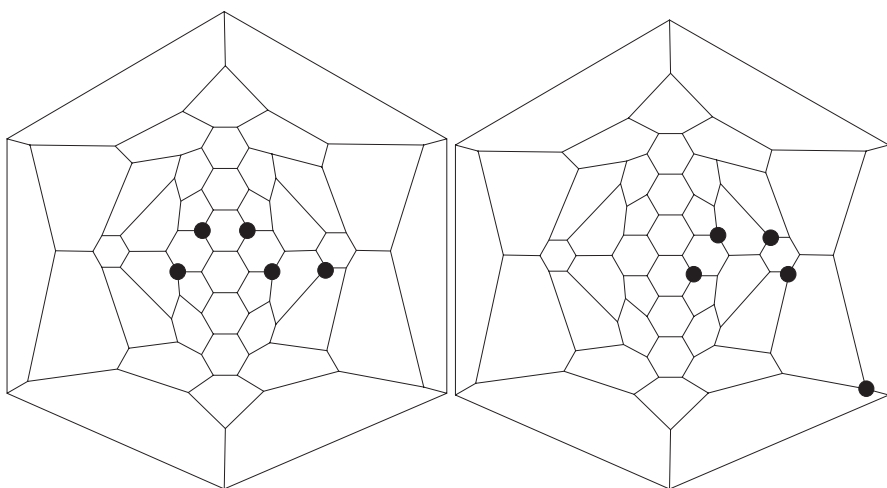


Figure 5. Schlegel diagrams of the most stable isomers for $Y@C_{82}(CF_3)_5$.

4. Conclusion

In summary, we (i) demonstrated an efficient method for the exohedral derivatization of the EMFs $M@C_{82}$ ($M = Y, Ce$), (ii) isolated and characterized two stable diamagnetic isomers of $Y@C_{82}(CF_3)_5$ and three stable diamagnetic isomers of $Ce@C_{82}(CF_3)_5$, (iii) using 1D and 2D ^{19}F NMR spectroscopy suggested the topology of the CF_3 groups to the carbon cage of the EMFs molecule; (iv) showed that for mono-EMFs $M@C_{82}$ ($M = Y, Ce$), the nature of a metal atom does not affect a number of CF_3 groups added; (v) found that di-EMF $Ce_2@C_{80}$ does not form trifluoromethyl derivatives in contrast to di-EMF $Y_2@C_{80}$, which allowed $Y_2@C_{80}(CF_3)_n$ ($n = 1, 3$) to be synthesized.

Acknowledgements

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SYNTHESIS, ISOLATION AND SPECTROSCOPIC STUDY OF A SERIES OF ENDOHEDRAL METALLOFULLERENES $Y_2@C_{84}$, $Ce_2@C_{78}$ AND $M@C_{82}$ ($M = Y, La, Ce, Gd$)

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Abstract. The synthesis, isolation and multistage chromatographic separation of the $Y_2@C_{84}$, $Ce_2@C_{78}$ и $M@C_{82}$ ($M = Y, La, Ce, Gd$) was carried out. All these newly synthesized metallofullerenes are characterized by S_8 -MALDI mass spectrometry and UV-vis-NIR absorption spectroscopy.

Keywords: Fullerene; Arc discharge; Chromatography, Mass spectroscopy; Adsorption properties

1. Introduction

Endohedral metallofullerenes (EMFs), $M@C_{2n}$, are carbon cluster compounds containing one or more metal (M) atoms inside the fullerene cage C_{2n} [1]. The unique structure of EMFs and a great variety of their physical and chemical properties depending on metal inserted into the cage were of great interest. EMFs are materials promising for advanced technologies. They can be used as molecular conductors, magnets, and ferroelectrics, radiopharmaceutical preparations, and contrast agents for NMR tomography [1,2,3]. Recent investigations showed that EMFs could be used very efficiently in radiotherapy and tomography [4].

The feature of band structures of EMFs related to metal valence electron transfer to the fullerene cage fundamentally affects their properties. For example, EMFs involving metal atoms of the III group exhibit paramagnetic properties since the encapsulated metal (III) atom transmits three electrons to the fullerene cage. In the case of $La@C_{82}$, three valence electrons of La ($5d^1 6s^2$) are transferred to fullerene to form a $La^{3+}@C_{82}^{3-}$ complex, and an octet signal is observed in the EPR spectrum [1]. On the contrary, EMFs comprising two metal (III) atoms become diamagnetic ones since two encapsulated metal atoms transmit three electrons to the fullerene cage to form a $M_2^{6+}@C_{2n}^{6-}$ complex [5,6]. As a result, spin moments of valence electrons, which occupy outer orbitals of the fullerene cage are fully compensated to produce no EPR

signal. Nevertheless, it is possible to study the structures of these compounds using NMR spectroscopy [7].

In this report, we present the first successful production, separation, isolation, and UV-vis-NIR absorption spectroscopic characterization of $Y_2@C_{84}$ and $Ce_2@C_{78}$. The separation and the isolation of $M@C_{82}$ ($M = Y, La, Ce, Gd$) are also described.

2. Experimental

EMFs-containing soots were synthesised in an electric reactor by a DC arc-discharge method. The design of the reactor was described in our previous papers [8,9]. Y-, La-, Ce- and Gd- composite graphite electrodes of analytic grade were used to obtain EMFs. A hole (3 mm in diameter) was drilled in the centre of a graphite rod (6 x 160 mm). Metal hydride powders (YH_3 , LaH_3 , CeH_3 and GdH_3) were mixed with graphite powder and graphite cement (GCS trademark, Dylan Industries Inc.) as a binder. The prepared mixture was thoroughly stirred, and then packed in the hole of the graphite electrode. The M/C ratio ≈ 1.0 at. % was found to be the optimal for the EMFs formation. The modified electrode rods were thermally treated in three stages: 1) treatment in a vacuum furnace at 130 °C for 4-5 h; 2) heating in vacuum (10^{-3} Torr) at 1100 °C for 4 h; and 3) thermal treatment directly in a reactor in vacuum (10^{-3} Torr) at 1800 - 1900 °C for 1 h; temperature was attained by passing 190 - 200 A direct current through the electrodes. The optimal conditions of arc evaporation of the electrodes were the following: helium pressure - 120 Torr, direct current – 80-90 A, voltage - 25-30 V, arc length - 5 mm, the distance between arc and a cooled wall of the reactor - 50 mm, evaporation rate - 1 mm/min.

EMFs were isolated from soot using extraction with boiling *o*-dichlorobenzene (DCB) (≥ 99 %, Aldrich) in argon atmosphere. Then the solution of EMFs and empty fullerenes was thoroughly filtered off, and the solvent was removed in a rotor evaporator. The resulting solution was filtered off, the solvent was evaporated, and the residue was dried at 90 °C for 1 h in vacuum.

For the isolation of pure EMFs $Y_2@C_{84}$, $Ce_2@C_{78}$ and $M@C_{82}$ ($M = Y, La, Ce, Gd$), a two-stage chromatographic procedure was developed. DCB extracts were dissolved in xylene, filtered using a 0.45 μm filter to remove insoluble impurities. In the first separation stage, Cosmosil Buckyprep (20 mm i.d. $\times$ 250 mm, Nacalai Tesque Inc.) (18 mL injections, 18 mL/min flow rate, toluene eluent) was used. In the second stage, Regis Buckyclutcher (20 mm i.d. $\times$ 250 mm, Regis Chemical Co.) (0.6 mL injections, 12 mL/min flow rate, toluene eluent) was applied for the isolation of pure EMFs $Y_2@C_{84}$, $Ce_2@C_{78}$ and $M@C_{82}$ ($M = Y, La, Ce, Gd$).

The mass spectrometry analysis was performed by the matrix assisted laser desorption/ionisation time-of-flight (S_8 -MALDI) technique using a Voyager-DETM PRO BiospectrometryTM Workstation (Applied Biosystems, USA). Radiation pulses of 0.5 ns and 3 Hz frequency from N_2 laser operating at 337 nm were used to desorb the species and negative/positive ions formed were detected in reflectron mode. Sulfur used as a matrix material was also dissolved in toluene and mixed with the samples solution prior to deposition onto a target.

The UV-vis-NIR spectra of isolated EMFs were recorded between 300 and 1100 nm in a toluene solution using a Varian Cary 500 Scan UV-Vis-NIR – spectrophotometer.

3. Results and Discussion

3.1. SYNTHESIS OF EMFs-CONTAINING SOOTS

Composite graphite electrodes based on metal hydrides (YH_3 , LaH_3 , CeH_3 and GdH_3) were for the first time used in the synthesis of EMFs containing soot. The use of metal hydrides instead of metal sward afforded electrodes with metals more homogeneously distributed in a graphite rod that provided more stable electric arc evaporation of electrodes.

It was found that the yield of DCB extracts of $\text{C}_{2n}/\text{M}@\text{C}_{82}$ ($\text{M} = \text{Y}, \text{La}, \text{Ce}, \text{Gd}$) from soot obtained by evaporation of composite electrodes based on YH_3 , LaH_3 , CeH_3 or GdH_3 is 2-3 % higher (4-5 wt. % of the primary soot) than the yield of the extracts from soot synthesized using the electrodes based on metallic yttrium, lanthanum, cerium or gadolinium. The extracts were studied using S_8 -MALDI and HPLC. Figure 1 shows the mass-spectra and the HPLC trace of the DCB extracts of $\text{C}_{2n}/\text{Ce}@\text{C}_{2n}$.

3.2. SEPARATION AND ISOLATION OF EMFs $\text{Y}_2@\text{C}_{84}$, $\text{Ce}_2@\text{C}_{78}$ AND $\text{M}@\text{C}_{82}$ ($\text{M} = \text{Y}, \text{La}, \text{Ce}, \text{Gd}$)

In the first stage of HPLC (Fig. 1a), the solution of DCB extracts of EMFs of $\text{C}_{2n}/\text{Ce}@\text{C}_{2n}$ in xylene was separated in a Cosmosil Buckyprep column. This stage allows the fraction containing $\text{Ce}@\text{C}_{82}$, $\text{Ce}_2@\text{C}_{78}$ and C_{88} (fraction A) to be separated from C_{60} , C_{70} and higher fullerenes (C_{76} - C_{110}). In the second stage (Fig. 2), a Regis Buckyclutcher was used to isolate individual $\text{Ce}@\text{C}_{82}$ and $\text{Ce}_2@\text{C}_{78}$ from fraction A. The separation procedure was repeated 2-3 times in Regis Buckyclutcher column to attain high purity of the samples. The isolation of other EMFs was performed using the above described scheme. Figures 3 and 4 (inset) show the S_8 -MALDI mass spectra of pure EMFs: $\text{Ce}_2@\text{C}_{78}$ and $\text{Y}_2@\text{C}_{84}$. The spectra show only the peaks with $m/z=1216$ and $m/z=1186$ attributable to $\text{Ce}_2@\text{C}_{78}^+$ and $\text{Y}_2@\text{C}_{84}^+$ ions, respectively. According to the data of HPLC and S_8 -MALDI, all isolated EMFs were of ~ 99% purity.

3.3. UV-vis-NIR ELECTRONIC ABSORPTION SPECTROSCOPY

The UV-vis-NIR absorption spectra of newly isolated EMFs $\text{Ce}_2@\text{C}_{78}$ and $\text{Y}_2@\text{C}_{84}$ were recorded between 300 and 1100 nm in toluene solution. The spectrum of $\text{Y}_2@\text{C}_{84}$ (Fig. 4) is remarkably rich with characteristic absorption bands at 355, 482, 625, 710 and 785 nm. The onset of the absorption spectrum is at 785 nm and corresponds to the lowest energy electronic transition approximately the HOMO-LUMO energy gap. Figure 3 shows the UV-vis spectra of $\text{Ce}_2@\text{C}_{78}$ with several

characteristic absorption bands at 387, 515, 555, and 637 nm, with an onset around 1000 nm. The spectrum is similar to the UV-vis-NIR spectrum of $\text{La}_2@\text{C}_{78}$ with molecular symmetry $D3h\text{-C}_{78}(78:5)$ [10]. The UV-vis-NIR spectra of $\text{M}@\text{C}_{82}$ ($\text{M} = \text{Y}, \text{La}, \text{Ce}, \text{Gd}$) are identical to those in toluene reported in [1].

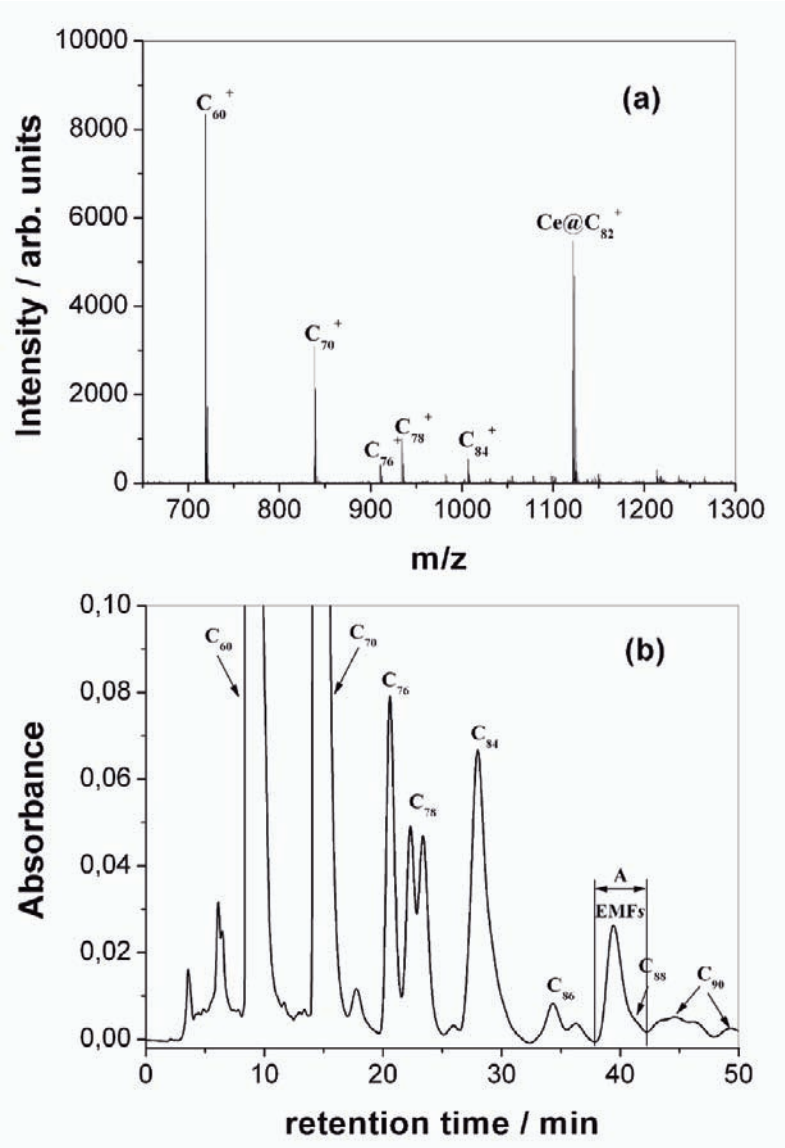


Figure 1. (a) Positive-ion S_8 -MALDI mass spectrum of DCB extracts of $\text{C}_{2n}/\text{Ce}@\text{C}_{2n}$; (b) HPLC traces (Cosmosil Buckyprep column) of the DCB extracts of $\text{C}_{2n}/\text{Ce}@\text{C}_{2n}$.

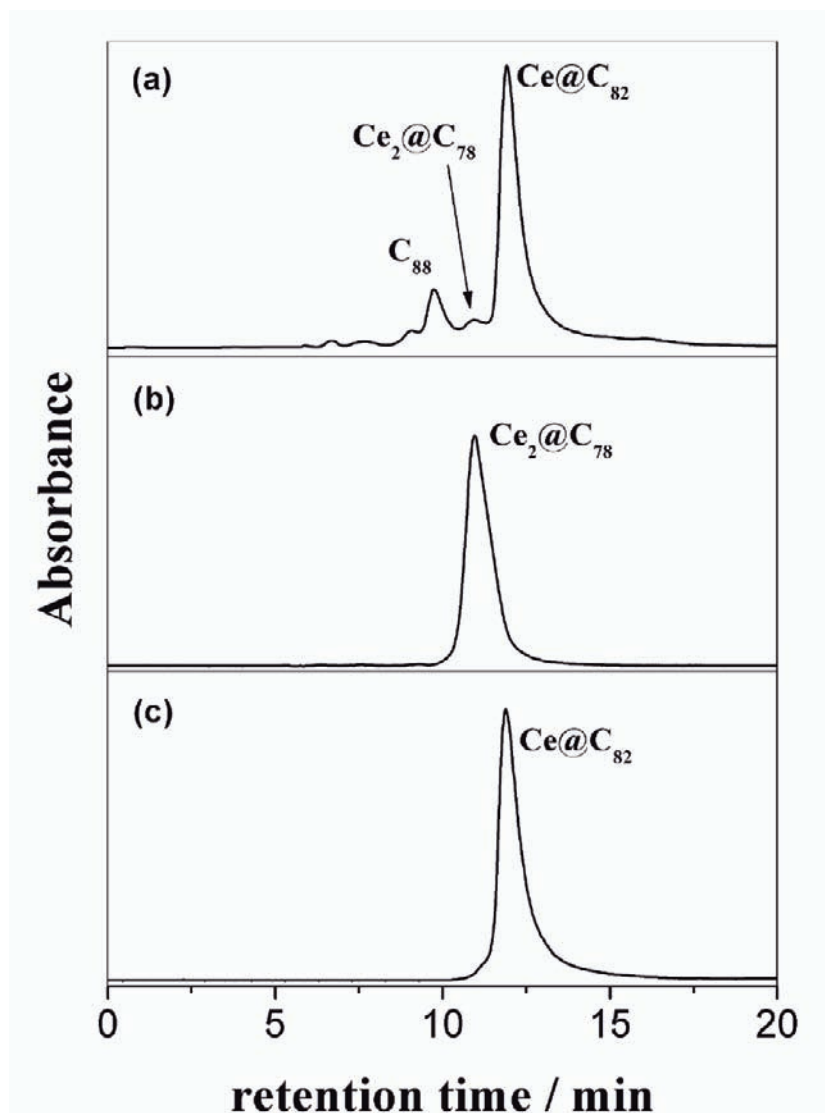


Figure 2. HPLC traces (Buckyclutcher column) of fraction A (a), purified sample of $Ce_2@C_{78}$ (b), purified sample of $Ce_2@C_{78}$ (c).

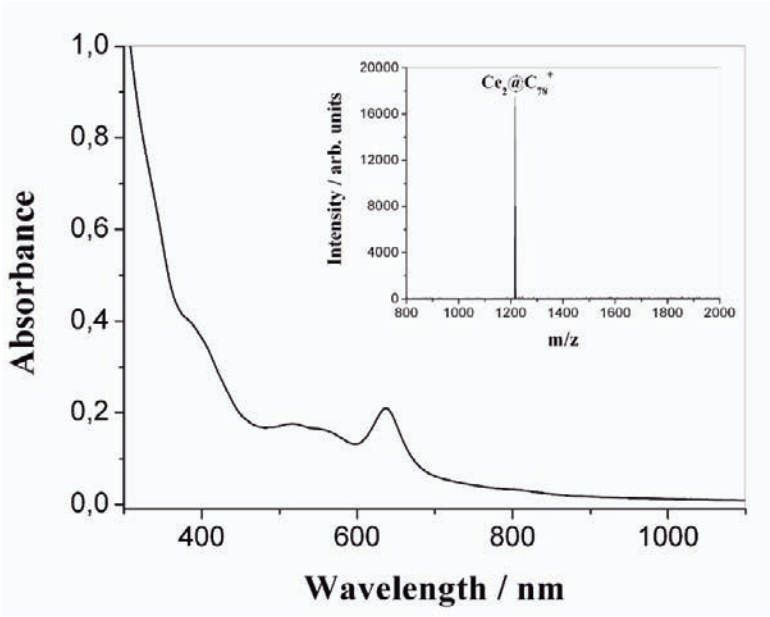


Figure 3. UV-vis-NIR spectrum of HPLC-purified Ce₂@C₇₈. The inset shows the positive-ion S₈-MALDI mass spectrum of HPLC-purified Ce₂@C₇₈.

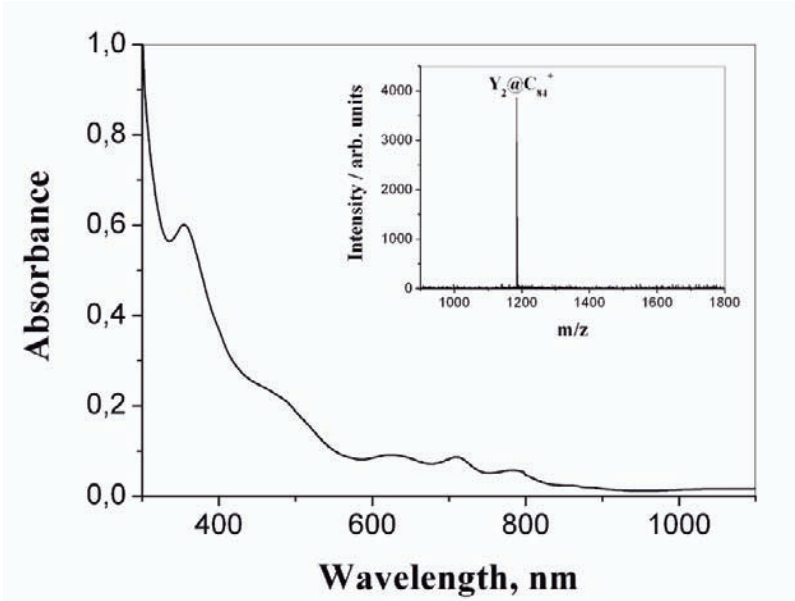


Figure 4. UV-vis-NIR spectrum of HPLC-purified Y₂@C₈₄. The inset shows the positive-ion S₈-MALDI mass spectrum of HPLC-purified Y₂@C₈₄.

4. Conclusion

For the first time the possibility of the use of metal (La, Y) hydrides to prepare composite graphite electrodes was studied. The yield of DCB extracts of $C_{2n}/M@C_{82}$ ($M = Y, La, Ce, Gd$) from soot obtained by evaporation of composite electrodes based on YH_3 , LaH_3 , CeH_3 or GdH_3 is 2-3 % higher (4-5 wt. % of the primary soot) than the yield of the extracts from soot synthesized using the electrodes based on metallic yttrium, lanthanum, cerium or gadolinium. EMFs $Y_2@C_{84}$ and $Ce_2@C_{78}$ were produced, separated, and isolated for the first time. Their purity was justified by S_8 -MALDI mass spectrometry and they were characterized by UV-Vis-NIR absorption spectroscopy.

Acknowledgements

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FORMATION OF ORDERED CARBON NANOSTRUCTURES AT PYROLYSIS OF HYDRATED CELLULOSE CONTAINING THE METALS OF FERROUS SUBGROUP

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Abstract. The influence of the additions of the metal salts of the ferrous subgroup on the process of carbonisation of hydrated cellulose fibers has been investigated and the structure of obtained Me-carbon fibers has been studied. It is established that the presence in the hydrated cellulose fibers such salts as nickel chloride and nickel, cobalt and ferric nitrates promote the formation of structure ordered carbon phases at the process of carbonisation.

Keywords: carbon fibers, carbonisation, metallic catalysts, ordered carbon, x-ray diffraction.

I. Introduction

The metals of ferrous subgroup and their alloys are usually used as the catalysts in processes of formation ordered carbon nanostructures [1]. There is a clear correlation between the sizes of catalyst particles and the tipe of carbonic deposits on their surface.

It is known many ways for obtaining of catalytic nanosize systems. The pyrolysis of systems *polymer - salt* is one of them. During this process the salts are reduced up to free highly disperse metal particles. These particles are then the catalysts of process of carbon nanostructures formation.

At the present work the process of carbon structuring is studied at carbonization in temperature of heat treatment (THT) 400-900 °C of hydrated cellulose (HC) fibres, impregnated by the salts of metals of ferrous subgroup, that was resulting to formation of metal-carbon fibres (Me-CF).

2. Experimental

The conditions of carbonization, and also the methods of thermal, electron microscopy, IR and X-ray diffraction researches are described in [2].

It is established, that during the carbonization of systems *HC- salt of metal of ferrous subgroup* the reducing of the salts to the free metals take place. These highly disperse metals catalyze (at definite THT) the processes of carbon structuring with formation of different phases of ordered carbon. On literary data

[3], the different mechanisms of the growth of ordered carbon nanostructures on the surface of metallic catalysts are characterized by three common stages: the dissolving of carbon in metal, the formation of carbon nucleating centre on the surface of metal particle and the growth of carbon nucleating centre resulting in to the formation of different carbon products. The size of the carbon nucleating centre determines the sizes of carbon deposits formed on the surface of the catalytic particles. So, at the large sizes of a critical nucleating centre (radius $r > 10\text{-}20\text{ nm}$) the extended carbon layers are formed, which capsulate the metal particles, and/ or the carbon nanofibers are obtained. When the small-size multiple nucleating centres ($r \approx 0,35\text{-}1,5\text{ nm}$) are arised on a metal surface, the bundles of single-layer carbon nanotubes are formed. In the case of the intermediate sizes of a critical nucleating centre there is a formation of more or less ordered coaxial cylindrical structures, including multilayer carbon nanotubes. In our case on the base of the data of electronmicroscopy and X-ray diffraction analysis it is possible to conclude, that on a surface of metal particles in the structure of Me-CF the turbostrate carbon with $d_{002} = 0,344\text{ nm}$ and graphitic nanofibers with $d_{002} = 0,337\text{ nm}$ are formed, the dimentionions of the areas of coherent diffraction (ACD) on the axis c and a are $6,3\text{ nm}$ (L_c) and $22,8\text{ nm}$ (L_a) accordingly (Table I). In addition that the capability of the formation of other carbon nanostructures is not excepted.

At the work it is established that the morphological and crystallographic characteristics of the formed nanostructures and also the initial temperature of their formation depend on the conditions of Me-CF obtaining and cationic-anionic structure of the salt additions introduced into the initial HC fibers. So, at the pyrolysis of HC with the additions of ferric and cobalt chlorides the carbon structuring does not occur: amorphous carbon are formed in all studied intervals of THT.

The formation of structure ordered carbon phases with $d_{002} = 0,344; 0,337\text{ nm}$ take place at pyrolysis of HC with the additions of NiCl_2 , $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$. The temperature of begining of the structuring for each system is various. So, in a system HC-Fe (NO_3)₃ the appearance of the carbon ordered phases take place at THT $600\text{ }^\circ\text{C}$, in systems HC-Ni(NO_3)₂ and HC- NiCl_2 - at $800\text{ }^\circ\text{C}$, in a system HC-Co (NO_3)₂ - at $900\text{ }^\circ\text{C}$.

The appearance of new phases of structure ordered carbon is accompanied by the fall of Me-CF strength (Table 2) and by the development of a porosity. The sorbate volume of pores in the samples of Me-CF with THT above $800\text{ }^\circ\text{C}$, which was determined by the sorption of benzene, makes $0.13\text{-}0.16\text{ cm}^3\cdot\text{g}^{-1}$ for chlorides and $0.11\text{-}0.26\text{ cm}^3\cdot\text{g}^{-1}$ for nitrates.

The availability of highly disperse metals and developed specific surface in the structure of Me-CF opens the capabilities for usage of Me-CF as active catalysts of chemical processes, including the processes for obtaining of nanostructured carbon.

TABLE 1. Relation of change of intensity (I), interplanar spacing interval (d_{002}), medium dimensions of ACD (L_c , L_a) for coal rest obtained after heat treatment of hydrated cellulose with the additions of the metal salts of ferrous subgroup

Sample	THT, °C	I, Arb. un.	d_{002} , nm	L_c , nm	L_a , nm	I, Arb. un.	d_{002} , nm	L_c , nm	L_a , nm
		The first component				The second component			
HC	800					41	0.386	1.0	3.6
HC -Fe(NO ₃) ₃	600	26	0.337	6.3	22.7	14		2.9	10.4
HC - Fe(NO ₃) ₃	800	56	0.337	6.3	22.7	16	0.344	2.2	7.9
HC -FeCl ₃	600					A broad halo			
HC -FeCl ₃	800					30	0.386	1.1	3.9
HC -Co(NO ₃) ₂	600					Amorphous			
HC -Co(NO ₃) ₂	900	18	0.337	6.3	22.8	16	0.344	1.1	3.2
HC -CoCl ₂	600					Amorphous			
HC -CoCl ₂	800					Amorphous			
HC -Ni(NO ₃) ₂	600					Amorphous			
HC -Ni(NO ₃) ₂	800	28	0.337	6.3	22.8	A broad halo			

TABLE 2. Dependence of the break strength of Me-CF from the temperature of heat treatment

Sample	The break strength (MPa) at different THT					
	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
HC		110	80	100	110	125
HC -Co(NO ₃) ₂	90	80	60	40	35	20
HC -CoCl ₂	92	70	60	50	30	30
HC -Ni(NO ₃) ₂	300	240	240	270	200	80
HC -NiCl ₂	820	740	710	700	790	100

3. Conclusions

The catalytic influence of metals of the ferrous subgroup on the process of carbon structuring in carbonised HC is established. The influence of anionic structure of introduced salts on the process of the HC thermal decomposition and following transformations in the system *metal - carbonic rest* are shown. The obtained results present both scientific and practical concern at creation of catalysts for obtaining of nanostructured carbon.

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NEW DESIGN OF ELECTRON GUN FOR FIELD EMISSION LIGHT SOURCES WITH CARBON FIBERS CATHODE

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Abstract. This work is devoted to development of the effective electron gun for the triode light sources. The electron gun is based on field emission cathode made of a bundle of PAN carbon fibers encapsulated into a glass capillary. The complex of researches on optimization of electron-optical system has been carried out.

Keywords: Field emission, carbon fibers, plasmachemical treatment, light source, electron-optical system

1. Introduction

An efficiency of the cathodoluminescent light source depends directly from the efficiencies of its basic components: an electron gun and luminescent covering. The diminishing of the power consumption and the increasing of the cathodoluminescent lamps efficiency are provided with application of field emission cathodes made of carbon fibers.

Such field emission cathodes require no heating, they are not inertial. These cathodes are stable against temperature fluctuations, and they possess a high density of field emission current and a high slope of current-voltage characteristics. The field emission cathodes based on carbon fibers have a sustained performance in conditions of technical vacuum ($\sim 10^{-4}$ Pa).

The purpose of the current work is the development of the effective electron-optical system for the cathodoluminescent light source with the field emission cathode based on polyacrylonitrile (PAN) carbon fibers [1].

2. Experimental

The electron-optical system of the cathodoluminescent lamp consists of electron gun and luminescent screen, which is covered by phosphor. It represents the triode construction. The base of this triode is the cathode-modulator unit (CMU) that consists of field emission cathode and extraction electrode (modulator).

The field emission cathode is made of PAN carbon fibers bundle encapsulated into the glass capillary. The diameter of the single fiber is $7\text{ }\mu\text{m}$ (the bundle contains about 300 fibers).

The anode of the lamp is supplied with positive high voltage $+U_A$. The cathode potential is grounded, and the modulator is supplied with positive control voltage. Electrons are extracted by the modulator and accelerated by the anode voltage. Phosphor glows under the influence of high-energy electrons.

The electron-optical system of a lamp should provide high operating ratio of field emission current emitted by the cathode. Earlier the prototype design of the

electron gun with field emission cathode based on a bundle of carbon fibers has already been presented [2]. The first disadvantage of that electron gun was a sufficient modulator current (10-20% of the total current from the cathode).

In other words a considerable portion of electron flow from the cathode come upon the control electrode (Fig. 1*a*), decreasing the efficiency of electron projector. And the second disadvantage is that operating voltages of the control electrode were sufficiently high (in the range 1.5-2.0 kV).

In order to increase the efficiency of electron projector a modernization of the cathode-modulator unit of the lamp was carried out. The new design of electron gun was offered (Fig. 1*b*). It possesses the higher transmission of the cathode current (the modulator current is less than 1% of total cathode current) against the prototype design of CMU, where the essential portion of electrons is certainly held up by the control electrode.

The current-voltage characteristics for the electron gun with the prototype (Fig. 2*a*) and the new (Fig. 2*b*) CMU design were measured. As one can see, at the anode voltage +10 kV (an operation mode for the cathodoluminescent lamps) the maximum value of the modulator voltage is 1200-1300 V (at the cathode current 100 μ A).

3. Forming the emitting surface of field emission cathode made of carbon fibers bundle

Creation of the advanced emitting surface of the field emission cathode is provided not only by an internal structure of carbon fibers, but also by corresponding preliminary forming of the cathode.

It is necessary to shape the carbon fibers bundle into such geometrical form, which would provide a maximum quantity of the emission tips in regular intervals located on its surface giving about the identical contribution to the general field emission current.

Using the plasmachemical method [3] of etching it was possible to receive the corresponding structure of carbon fibers bundle.

The carbon fibers bundles structures of the raw cathode and the cathode etched by the plasmachemical method are represented in Fig. 3. Their corresponding field emission images are also presented there.

At plasmachemical etching process the carbon fibers bundle gets the rounded form: prominent fibers are absent, and peripheral — are short. At that time the uniformity of the luminescent screen radiation essentially improves.

The obtained data testify that the much greater number of fibers works, and the field emission tips after the forming process are distributed more regular on the surface of the cathode.

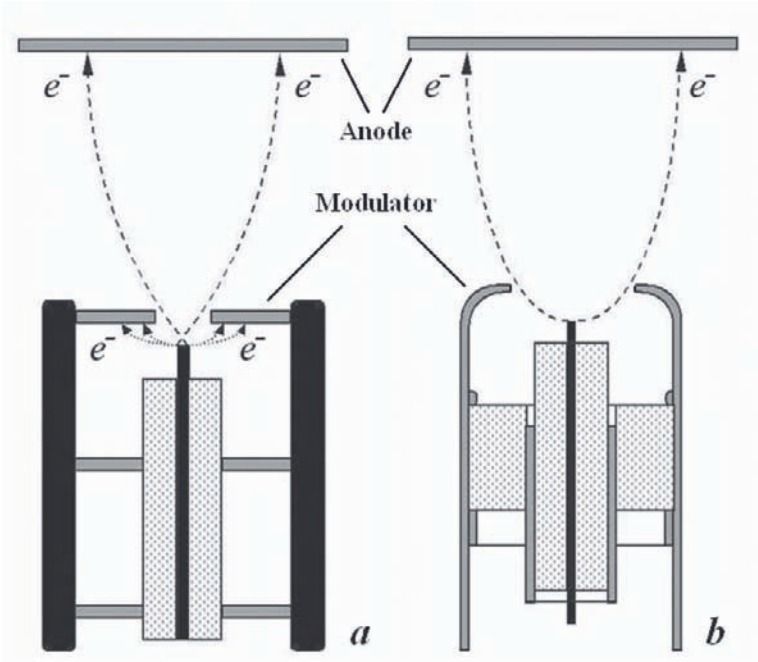


Figure 1. Cathode-modulator unit: *a* — prototype design; *b* — new optimized design.

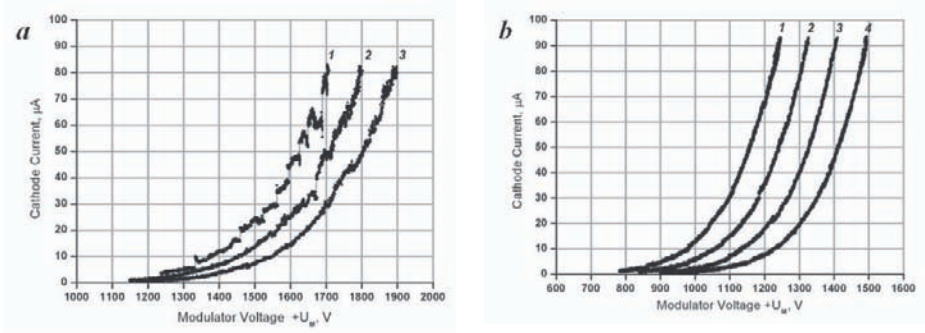


Figure 2. The dependence of the cathode current on the voltage of control electrode for the CMU of the prototype design (*a*) and the new optimized design (*b*) at different anode voltages: 1 — $U_A = +10$ kV, 2 — $U_A = +9$ kV, 3 — $U_A = +8$ kV, 4 — $U_A = +7$ kV.

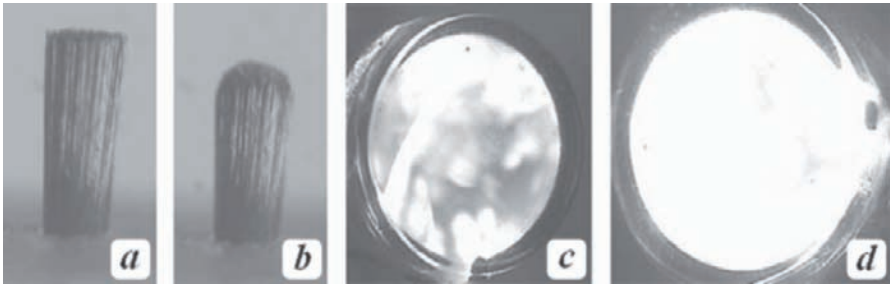


Figure 3. The non-forming carbon fibers bundle (a) and its field emission image (c). The carbon fibers bundle etched by plasma-chemical method (b) and its field emission image (d).

4. Conclusions

The effective electron-optical system with the field emission cathode based on PAN carbon fibers is developed. Modernization of electron gun design has allowed to decrease operating voltages of the light source essentially and to enhance the cathode current transmitting.

The decrease of operating voltages down to a level less than 1500 V specifies an opportunity of developing the control circuit with use of existing high-voltage transistors.

The uniformity of the field emission image was greatly improved by means of preliminary plasma-chemical processing of carbon fibers bundle.

Acknowledgements

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PHYSICAL PROCESSES ON THE SURFACE OF FIELD EMISSION CATHODES BASED ON CARBON NANOSTRUCTURAL MATERIALS

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Abstract. The degradation mechanism of field emission cathodes based on carbon nanostructural materials was investigated in the presented work. Emission current instability came from the adsorption desorption processes on the cathode surface. During the long-time tests the periodical variation of the electron work function (caused by switching on and off of the cathode) was detected. The numerical model was proposed to explain the experimentally observed variations of electron work function.

Keywords: Carbon nanotubes, Field emission, Degradation, Adsorption.

1. Introduction

At present time field emission cathodes based on different carbon nanostructural materials became popular. Lifetime is a very important characteristic of the field emission cathodes. Generally there are two main degradation stages for planar cathodes based on carbon materials such as nanotubes, nanohorhs, nanographites and so on [1-4]. First of them is characterized by a change of cathode work function. It results in significant variations of emission current and, therefore, in rapid cathode degradation. This stage ordinary takes place right after high voltage is applied between cathode and anode. Its duration doesn't exceed a several minutes. After that another stage is began. It is described by slow, practically linear, function during operation time. This stage is connected with decreasing emission area or number of nanopaticles.

In this work a physical processes, which lead to variations in cathode work function, is considered. Also the numerical model, which is described field emission cathode degradation due to these processes, is proposed.

2. Cathode producing and field emission tests

The screen-printing technique was used to make the field emission cathodes. The carbon powder was obtained in the arc discharge. It was mixed with an organic binder to form a paste, which contains more than 80% of multiwall carbon

nanotubes. The paste was drown through the mask to a glass substrate covered by ITO layer. The area of the cathode was $0,125 \text{ cm}^2$. To remove the organic binder the cathode was baked out during 10 minutes at the 450°C .

The long-time test consisted of two periodic stages. During one of them the voltage between cathode and anode was applied. This stage is usually called an "operation stage". During another stage the cathode is not working, we call it "storage stage" (see Fig. 1). The long-term stability of the emission current in operation stage was investigated at the current stabilization mode. The applied voltage variations, which are required to keep a constant current, were measured.

During the entire long-time test (both operation and storage stages) the current voltage characteristics (I-V curves) were measured every 30 seconds. Then each I-V curve is represented in Fowler-Nordheim coordinates, where it could be interpolate by straight line $\ln(I/V^2) = A + B/V$. During the cathode operation, its parameters vary due to some physical phenomena such as ion bombardment and electrostatic force loads. We record those variations as dependence of parameters A and B in time.

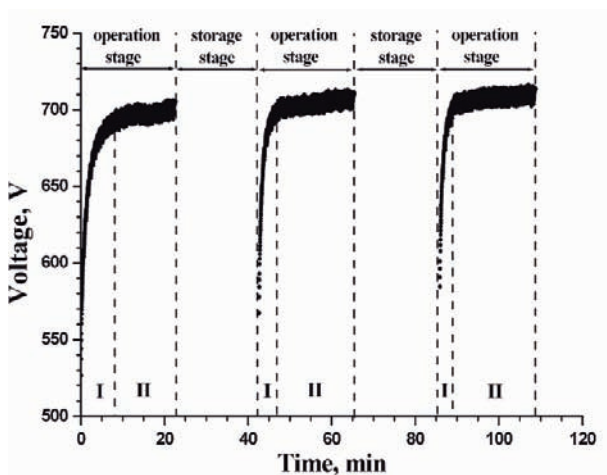


Figure 1. Voltage versus time at a constant current density $j = 0,5 \text{ mA/cm}^2$. The long-time test consisted of two periodic stages ("operation" and "storage"). During operation stage two degradation regions are presented (marked as "I" and "II").

3. The model of the adsorbed layer formation

Developed model is based on following assumptions. During storage time molecules of residual gases are adsorbed on a surface of the field emission cathode. Using results of the latest theoretical work [5, 6], in which the effect of different gases molecules adsorption on electronic properties of single carbon nanotube is considered, it is possible to assume that some molecules (with polar moment) adsorption is able to change a cathode work function. Then voltage is applied between cathode and anode, adsorption layer is destroyed due to ion bombardment.

At the same time the value of cathode work function is restored to its magnitude for clean carbon surface.

The numerical description of model is based on following key assumption. Adsorbed atoms on a surface of the field emission cathode can exist in two different states. In first state gas molecule is attracted to an adsorbent by only dispersion forces. The given state corresponds to a case of physical adsorption, which is characterized by relatively small bond energy U_{ph} of an adsorbent-adsorbed atom system. Also another process – chemical adsorption – is possible. In this case there is a partial interchanging by conduction electrons between an adsorbent and adsorbed atom, i.e. the strong chemical bond will arise. This state is characterized by activation energy U_{ch} . A threshold U_t characterizes transition from the physical adsorption state into the chemical adsorption state. The reverse process is neglected since $U_t > U_{ph}$. Thus the molecule desorbing from the chemical adsorption state has enough energy to go away from the surface instead of capturing to the physical absorption state. The potential energy of molecules at consistent transition from physical to chemical adsorbed states is shown on Fig. 2.

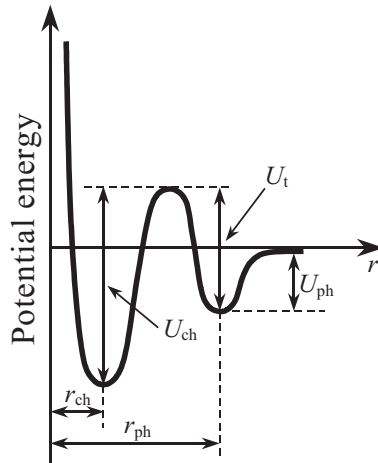


Figure 2. The potential energy of molecules at consistent transition from physical to chemical adsorbed states. U_{ph} is a bond energy in physical adsorption state, U_t is threshold energy and U_{ch} is activation energy of chemical adsorption state.

If voltage between anode and cathode is applied, ionized neutral molecules of residual gases are accelerated in an electrical field and bombard a cathode. Thus there is a clearing of a cathode surface from different films of oxides and impurities due to process of cathode sputtering depicted elsewhere [7, 8]. We consider that at ion impact in a cathode surface causes a rapid heating of some small cathode area, which results in local explosion. Thus the given surface area is completely (or almost completely) cleaned from adsorbed atoms. Then due to migration process the equilibrium distribution of gas particles on cathode surface is formed again. The characteristic time of such process is much lower, than time of thermal desorption as energy threshold at surface migration is below by several times than

one at adsorption (bond energy). Thus, it is possible to consider, that the ion bombardment uniformly cleans a cathode surface with large efficiency.

Using the above-mentioned assumptions one can write the system of equations characterizing coverage variation for storage stage:

$$\begin{cases} \dot{\Theta}_{ph} = K_a \frac{Z}{N_0} - \frac{\Theta_{ph}}{\tau_0} \left[\exp\left(-\frac{U_{ph}}{kT}\right) + \exp\left(-\frac{U_t}{kT}\right) \right], \\ \dot{\Theta}_{ch} = \frac{\Theta_{ph}}{\tau_0} \exp\left(-\frac{U_t}{kT}\right) - \frac{\Theta_{ch}}{\tau_0} \exp\left(-\frac{U_{ch}}{kT}\right) \end{cases}, \quad (1)$$

and for operation stage:

$$\begin{cases} \dot{\Theta}_{ph} = K_a \frac{Z}{N_0} - \frac{\Theta_{ph}}{\tau_0} \left[\exp\left(-\frac{U_{ph}}{kT}\right) + \exp\left(-\frac{U_t}{kT}\right) \right] - j_i \frac{D_{ph}}{N_0} \Theta_{ph} \\ \dot{\Theta}_{ch} = K_a \frac{Z}{N_0} - \frac{\Theta_{ph}}{\tau_0} \left[\exp\left(-\frac{U_{ph}}{kT}\right) + \exp\left(-\frac{U_t}{kT}\right) \right] - j_i \frac{D_{ph}}{N_0} \Theta_{ph} \end{cases}, \quad (2)$$

where Z is the average flow of the molecules per unit area in a unit of time; K_a is the accommodation coefficient or the probability for the molecule to be physically absorbed after impact on the surface; k is the Boltzmann constant; τ_0 is the period of the thermal oscillation; j_i is the ion flow to the unit area of surface; $\dot{\Theta}_{ph}$, $\dot{\Theta}_{ch}$ are the rate of changing of coverage and D_{ch} , D_{ph} are the spattering coefficients for the molecules in the physical and chemical adsorption states correspondingly.

Using published results [9], which describe the adsorption process of the active metal on the field emission cathodes surface, one can expect that only first several layers of the adsorbed atoms result in the significant changing of the electron work function in accordance with empirical formula

$$\varphi(\Theta_{ch}) = (\varphi_0 - \varphi_{min}) \exp\left(-\frac{\Theta_{ch}}{\Theta_{opt}}\right) + \varphi_{min}. \quad (3)$$

For our case $\varphi_0 = 4.7$ eV is the electron work function of the pure carbon nanotubes, φ_{min} is a minimum experimentally obtained value of electron work function of the carbon nanotubes with active coverage and Θ_{opt} is the optimum coverage.

4. Simulation results

To prove proposed model we estimate values of field enhancement factor, emission area and electron work function using experimental dependence of parameters A and B in time. These calculations are based on an assumption that the electron work function is equal to 4.7 eV (clean surface) at the end of the operation stage and field enhancement factor is constant (or its changes are negligible) during this stage. Calculated dependences of the electron work function and emission area during long-term test are represented on Fig. 3.

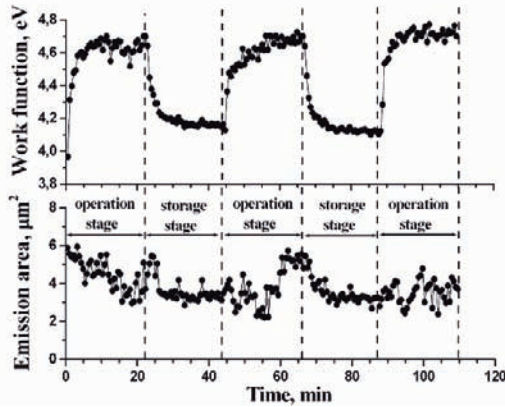


Figure 3. (a) Electron work function and (b) emission area variations during long-time test represented on Fig. 2.

Using the above-described model the numerical simulation of the electron work function variation during cathode operation and storage stages was carried out. For simulation bond energy U_{ph} in physical adsorption state is assumed to be equal to 0.5 eV, pursuant to value for oxygen [10]. Threshold energy U_t for the oxygen is 0.84 eV, and activation energy of chemical adsorption state $U_{ch} - 6$ eV [10]. To obtain a good agreement with the experimental results for storage stage we use as a fitting parameter a value of the optimal coverage Θ_{opt} in formula (3). Under our conditions this parameter is equal to about 1.6. To comply with experimental results for operation stage we choose values of sputtering coefficients so as the numbers of desorbed molecules per unit area due to the ion bombardment (parameter $j_i D$ in system (2)) are equal to $5 \cdot 10^{13}$ and $5 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ for physical and chemical adsorption states correspondingly at electron current $I_e = 70 \text{ mA}$. Simulated results in comparison with experimental data during storage and operation stages are presented in Fig. 4.

5. Conclusions

We found that there are two degradation regions for field emission cathode based on carbon nanotubes. The first of them is characterized by the great increasing of the operation voltage. This behavior of the cathode is connected with the destruction of the layer formed by adsorbed molecules, which leads to the change of the electron work function. Another degradation region is characterized by the slower changing of the operation voltage. This period is, probably, connected with the decreasing of emission area due to ion bombardment and electric field loads.

The physical model was proposed to describe the adsorption/desorption processes of the residual gases on the cathode surface. This model takes into account the destruction of the adsorbed layer due to the ion bombardment. The simulation results have a good agreement with the experimental data both on storage and operation stages. Moreover to prove an applicability of proposed model it should be emphasized that a single set of model parameters describe the behavior of the tested cathode under other experimental condition (current density, vacuum level and so on).

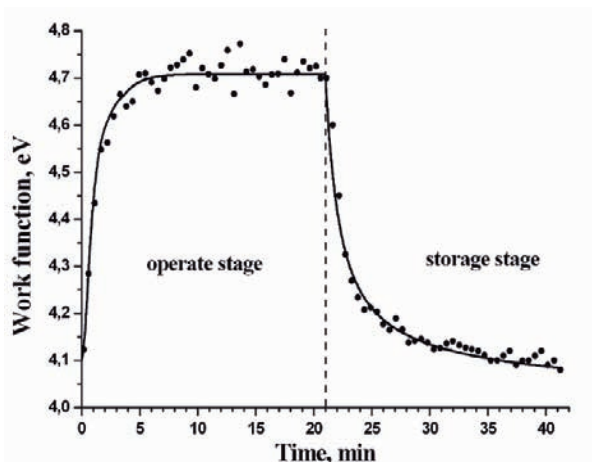


Figure 4. The electron work function variation during operation and storage stages. The solid line represents the simulation results (parameters are given in text); the black points – the values of the electron work function estimated from FN-charts, which are measured during long-time test.

Our preliminary tests show that the proposed model, probably, are applicable to field emission cathodes based on different carbon materials not only carbon nanotubes. However in order to define the applicability area of the proposed model it is necessary to carry out auxiliary investigations with other carbon materials.

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NEW TECHNIQUE OF FIELD EMISSION CATHODES PREPARATION BY LOW TEMPERATURE DEPOSITION FROM ETHANOL VAPOR

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Abstract. At this paper novel low temperature (temperature 500°C) deposition method for preparation of the carbon nanotubes cathodes is represented. This method allows to use a glass as cathode substrate. Investigated samples differ by geometry of deposited layer of the carbon nanotubes: with complete cover and cover with islands of different diameters.

Keywords: carbon nanotubes, chemical vapor deposition

1. Introduction

Process of chemical vapor deposition (CVD) is one of the most effective methods for preparation of flat emission cathodes. This method allows to produce different carbon structures on the cathode substrate. Depending on conditions of deposition, derivable carbon surface can be diamond-like films [1], amorphous graphite [2], various carbon constitutions, including carbon nanotubes [3]. Investigation results of field emission properties produced cathodes have shown this is a promising technology for production Field Emission Display (FED).

Majority of CVD technology require high temperature, making it impossible to use vacuum glass, as a substrate. Therefore one of the goals in research of production efficient flat emission cathodes is development of a low temperature synthesis technique.

Field emission cathodes described in this paper were produced by means of low temperature chemical vapor deposition method of carbon nanotubes from ethanol vapor. The substrate temperature during the deposition was 500 °C. This paper summarizes research results of prepared field emission cathodes.

2. Experiment

Low temperature chemical vapor deposition from ethanol was used for production of the samples. Selective deposition of carbon nanotubes took place under low temperature due to pyrolysis of ethanol vapor. Heating of substrate and pyrolysis of reagent vapor was done by a graphite heater, which was placed inside reactionary

space. The temperature of heater was varied in the range 1300 – 2200 °C. Substrate temperature was about 500 °C. Further description of this technology can be found in paper [4].

The substrate was usual 1.1 mm glass with sputtered aluminium layer. Ni was used as a catalyst. For optimization of cathode surface topography, three types of samples were prepared, with different catalyst distribution on the substrate. Catalyst layer in the first sample was uniform sputtered Ni layer. In the second and the third samples, the catalyst sputtering was produced through screens with 1 mm и 50 μm holes correspondingly. The distance between holes compared with the twice island diameter. The total area of each cathode sample was about 0.5 cm². Cathodes are shown on Fig. 1.

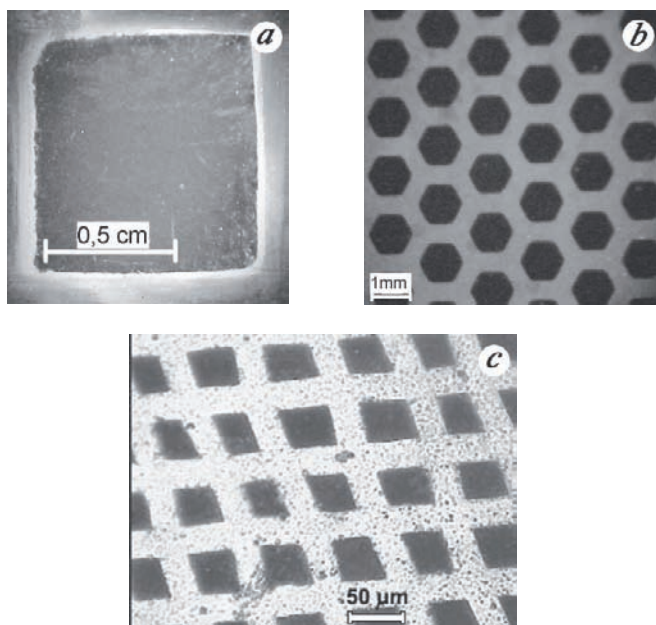


Figure 1. Investigated samples: *a* — sample with uniform layer of CNT, *b* — sample with islands of nanotubes with diameter 1 mm, *c* — sample with islands of nanotubes with diameter 50 μm .

Prepared cathode samples were tested in a diode structure. The glass plate with sputtered ITO layer was used as an anode. The distance between anode and cathode was setting by glass spacers and equals 200 μm . During the experiment the pressure of residual gas in the vacuum chamber was less than 3×10^{-7} Torr.

The special measuring bench was used for the investigation of cathodes field emission properties. This equipment allow to measure emission current from 0 to 1 mA with step 0.3 μA , voltage from 0 to 10 kV with step 2.3 V. Error of measurements does not exceed 1%.

Field emission cathodes were examined in the long duration mode for 10 hours under fixed value of current 50 μA . The test objective was in stabilization of the emission current value by means of the high-voltage power supply. During the experiment measurements of voltage, supplied on equipment, and emission were performed every second.

3. Results and discussion

Current voltage characteristic of examined samples before and after 10 hours of long duration test are shown on Figures 2 and 3 respectively.

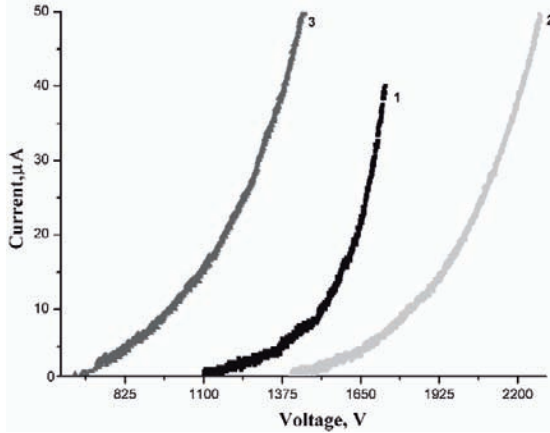


Figure 2. Current-voltage characteristic before long duration test: 1 — sample with uniform layer of CNT, 2 — sample with islands of nanotubes with diameter 1 mm, 3 — sample with islands of nanotubes with diameter 50 μm .

From diagrams on the Fig. 3 it is obviously, that the least threshold voltage (voltage needed for emission current is 1 μA) is 650 V for the sample with islands of nanotubes with diameter 50 μm . For the second and third samples the threshold voltage is higher 1100 V. This difference in the value voltage can be explained by the more optimal topography of surface the third cathode.

The developed structure allows getting the additional amplification of the electrical field on edges of islands.

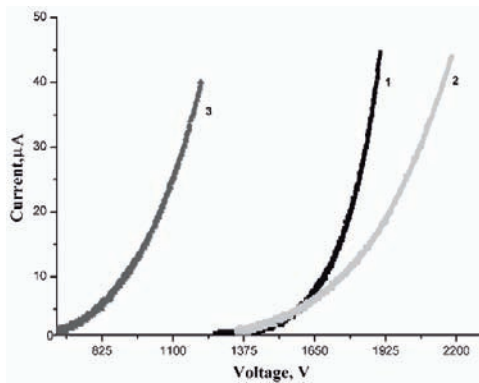


Figure 3. Current-voltage characteristic after long duration test: 1 — sample with uniform layer of CNT, 2 — sample with islands of nanotubes with diameter 1 mm, 3 — sample with islands of nanotubes with diameter 50 μm .

On Fig. 4 the graphs of the voltage-time dependencies are given for each of the samples. From this figure it is obviously that the samples with 50 μm islands subjected to degradation not observed with other samples.

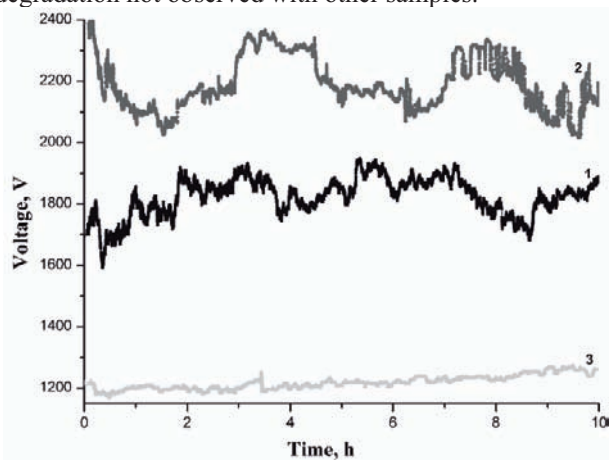


Figure 4. Voltage as a function of time.

Calculation of the current density, collected from samples, has shown that the current density of third type of samples is highest. The degradation of the cathode with islands of nanotubes with diameter 50 μm can be explained by the higher current on the emission centers.

4. Conclusions

Our experiment has demonstrated the possibility of the carbon nanotubes synthesis by low temperature (substrate temperature was 500°C) vapor deposition method from the ethanol vapor. Field emission samples were produced with different catalyst distribution on the substrate surface.

The field emission properties investigation has revealed that the cathodes with islands of nanotubes with diameter 50 μm have the best emission characteristics.

The results of cathodes stability investigation presented, that under current density, collected from cathode, less than 80 $\mu\text{A}/\text{sm}^2$, the tested cathodes are subjected unsubstantial changes of emission properties.

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FULLERENE SYNTHESIS IN HELIUM FLOW AT ATMOSPHERIC PRESSURE

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Abstract. We present results obtained on carbon structures formed as condensates from a carbon-helium plasma under atmospheric pressure, when the plasma is maintained by an alternating current (AC) of 44 kHz, of 50 Hz, and by direct current (DC), respectively. It was found that the kind of current (AC or DC) has no pronounced influence on the kind of produced substances (re-crystallized graphite, soot, fullerenes) but a significant influence on their relative abundance ratios. The relative abundances of the obtained fullerenes (C_{60} , C_{70} etc.) remain about constant independent of the kind of current applied. We observed that by applying AC of 44 kHz, the most efficient fullerene production was obtained in a chamber with diameter 20 cm and height 15 cm. Under these conditions, the plasma in the chamber is stratified, indicating that a kind of resonance is taking place which also may be responsible for the high fullerene productivity. No such effects occurred at AC or 50 Hz DC. At 44 kHz AC, the obtained productivity is 16 mg of soot per minute and the soot contains fullerene (9% weight) and the re-crystallized graphite (7%).

Keywords: arc discharge, fullerene, soot, recrystallized graphite, ionization wave

1. Introduction

Until now, the interest of the scientific community in fullerenes and their derivatives continues because of their interesting physical-chemical, optical, mechanical and electrical properties.

But a wide application of such substances is hampered by their high costs of synthesis and purification. The most popular synthesis methods are the arc-discharge and laser-ablation method which have the disadvantage of either small fullerene yield or small quantity of the fullerene containing soot. Moreover it is necessary to use vacuum technique for maintaining of low pressure of helium for these methods. For the hydrocarbon combustion method it is necessary to use the additional expenses for fullerene purification [1-3]. Thus, the search for improved methods of fullerene synthesis is of considerable importance.

In an earlier publication we showed that fullerene may be synthesized not only under low pressure conditions, but under atmospheric pressure as well [4]. In this work we present the result of fullerene synthesis by the arc discharge method under atmospheric pressure in which currents of different frequencies are applied.

2. Experimental

Fullerene synthesis was carried out in the arc between two graphite electrodes in the helium flow under atmospheric pressure. This arc was burning in the cylindrical chamber with diameter 20 cm and height 15 cm. The applied current was DC and AC with frequencies 50 Hz and 44 kHz. The evaporated carbon condensed on the chamber walls as fullerene containing soot and on the electrodes as re-crystallized graphite. Fullerenes were extracted from the soot by benzene. The quantity of synthesized soot, of re-crystallized graphite and of fullerenes was investigated as function of the synthesis parameters current value and electrodes feed-motion. The current was changed in the range of 50-230 A.

For characterization of the substances we used X-ray powder diffraction (DRON-4), HPLC (Shimadzu HPLC system with a Cosmosil Buckyrep column, eluent - toluene), and mass spectrometry (laser desorption time of flight mass spectrometer - Bruker BIFLEX). The study of the distribution of the plasma radiation intensity was carried out by the technique described in details in [5]. The emission of the discharge during one period of current was recorded many times on photo film using high-speed photo-registration setup having phase and frequency auto adjustment. The obtained images were fed into a personal computer and thus a section of the intensity distribution along the discharge height was plotted at an arbitrary time moment.

3. Results and Discussion

On the Fig. 1 the graphs of the obtained dependencies are shown. One can see that soot, fullerenes and re-crystallized graphite are formed in all cases, and their yields depend on both current value and current type. Re-crystallized graphite is a by-product of the fullerene synthesis which decreases the fullerene productivity and efficiency. It was established that the optimal regime of fullerene synthesis occurs at 44 kHz AC and 200 A. Under these conditions, a fullerene production rate of 16mg/min at a fullerene yield of 9% was obtained while the yield of re-crystallized graphite (7%) was minimal.

Our X-ray powder diffraction data show that the type and intensity of current had no influence on the re-crystallized graphite structure. The main part of this substance consisted of graphite with an increased distance between graphite planes ($3.42 \text{ \AA}$) [6].

It was found that the composition of the fullerene mixture obtained at different arc respectively plasma conditions did not changed significantly. The observed ratio of components ratio is displayed in Table 1 and Fig. 2.

The picture in Fig. 3 shows the plasma radiation intensity along the discharge as function of height during one period of current at 44 kHz AC. Against a background of periodical current one can observe non-uniform distribution of the radiation intensity not only along the time axis but along the discharge height as well. This feature indicates the presence of discharge stratification [5]. The strata can be viewed more distinctly on the radiation intensity profile (Fig. 4) along the discharge height. The strata frequency is equal to the double of the current frequency, i.e. 88 kHz. At the 50 Hz frequency of AC arc feeding the strata were not observed. In paper [7] was shown that the strata are exhibiting waves of electron concentration.

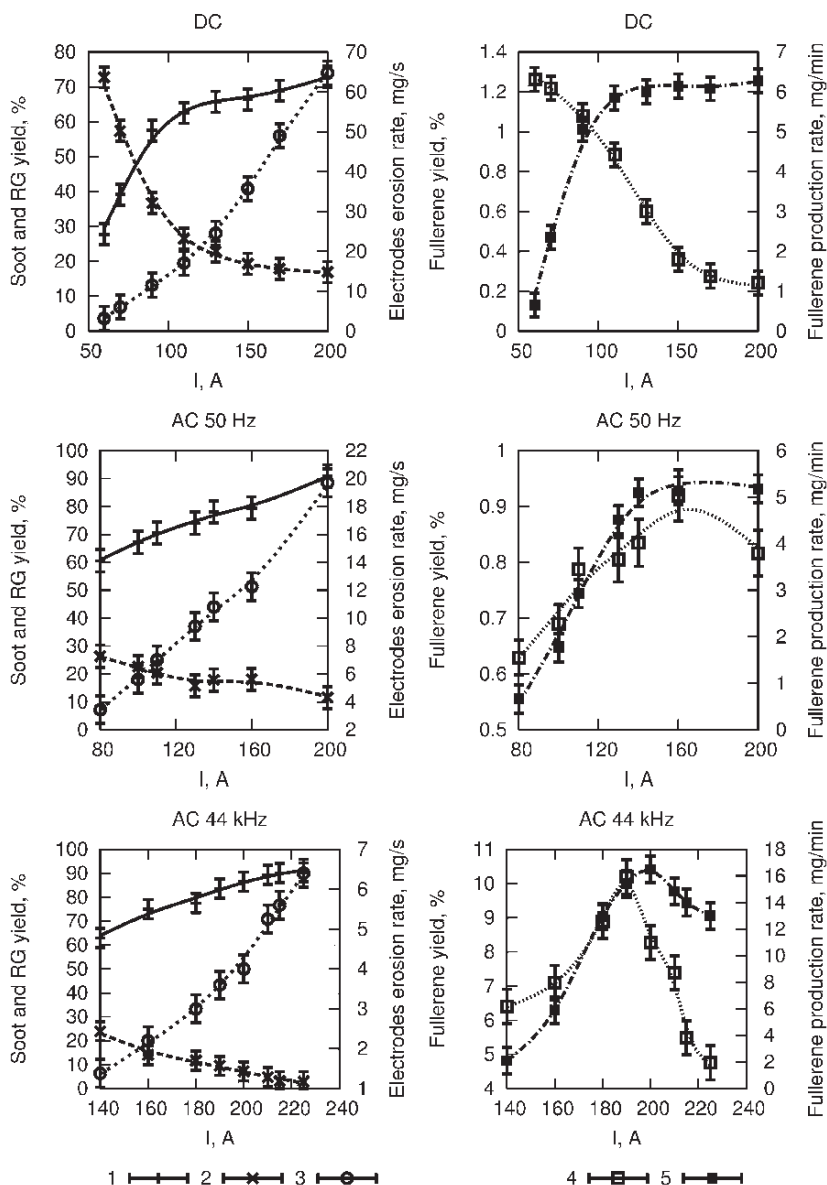


Figure 1. Dependencies of basic setup characteristics on arc current value for DC, AC 50 Hz, and AC 44 kHz: 1 – soot yield; 2 – recrystallized graphite (RG) yield; 3 – electrodes erosion rate; 4 – fullerene yield; 5 – fullerene production rate.

TABLE 1. Ratio of fullerenes formed in carbon-helium plasma at different current frequency

Type of current	C ₆₀ , %	C ₇₀ , %	C ₆₀ and C ₇₀ oxides, %	Highest fullerenes, %
DC	77	17	~1	~4
AC 50 Hz	84	13	<1	~3
AC 44 kHz	80	15	~1	~4

Thus, high fullerene yield at 44 kHz may be explained by the occurrence of electron concentration oscillations in the plasma. That such electron concentration oscillations are highly affecting the fullerene synthesis is known. For details see [8].

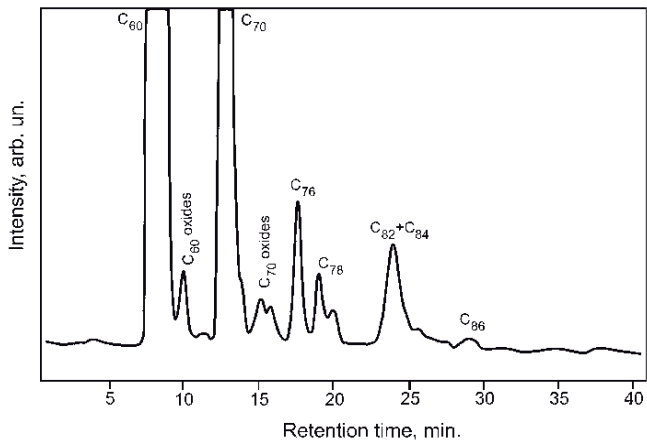


Figure 2. HPLC chromatogram of fullerene mixture synthesized at 44 kHz current frequency; registered at wavelength $\lambda=340$ nm.

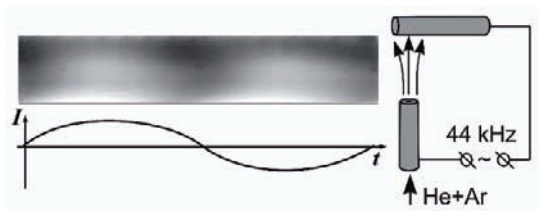


Figure 3. Photo scanning of plasma radiation intensity at 44 kHz frequency during one period of current. Corresponding graph of current variation is shown below. Scheme of electrodes positioning is shown on the right. r – distance between electrodes, I – current; t – time.

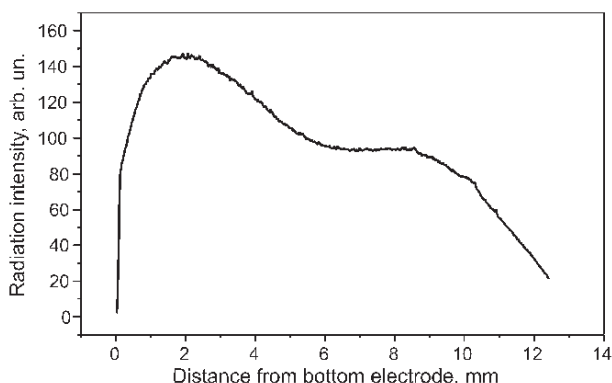


Figure 4. Profile of ionization wave presented in Fig. 3 (the place of section marked by “A” symbol)

4. Conclusions

The basic characteristics of devices for fullerene synthesis at atmospheric pressure were investigated. It was observed that the maximum fullerene production rate (16 mg/min) was obtained in arcs fed by AC of 44 kHz and 200 A. Under these conditions the amount of deposited re-crystallized graphite was minimal, and practically all evaporated carbon was transformed into soot containing 9% of fullerenes.

Acknowledgements

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ATOMIC HYDROGEN ADSORPTION ON BORON NITRIDE NANOTUBE SURFACES

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Abstract. Based upon the semi-empirical AM1 method, we have modelled the adsorption of a single hydrogen atom onto the outer surfaces of single-walled zigzag boron nitride nanotubes. Our calculations suggest that the H atom is adsorbed over N and B sites and predict that the adsorption on the top of the former is energetically more favorable than on the top of the latter. In addition, we present the calculated charge transfer from the adatom to the nanotubes, which can significantly affect the electronic properties of nanotubes.

Keywords: adsorption, boron nitride nanotubes, semi-empirical models and model calculations

1. Introduction

In the last years there has been an increasing interest in the study of boron nitride nanotubes (BNNTs), which are inorganic analogues of carbon nanotubes. This interest is partly motivated by the potential significance of these systems in the field of nanotechnology. In particular, similar to carbon nanotubes, BNNTs are thought to be promising materials for applications in hydrogen storage devices. Recently, several experimental and theoretical studies on hydrogen adsorption on BNNTs have been reported [1-5]. However, the specific features of the adsorption of a single H atom on BNNTs have not been clearly understood yet. In this connection, a more systematic study concerning this problem might be useful. In this report, we investigate the adsorption of a hydrogen atom on the outer surface of single-walled BNNTs through the semi-empirical AM1 (Austin Model) calculations. Our primary objective is to identify the preferable adsorption sites and to determine the adsorption energies for different BNNTs. We confine our consideration to the BNNTs with the chiral index $(n,0)$, since experimental investigations have shown that BNNTs tend to have a zigzag structure during their growth.

2. Results and Discussion

In order to carry out a meaningful computer calculation of the adsorption process of atomic H on the sidewall of the zigzag BNNTs $(n,0)$, we have assumed that the ends of the tubes are terminated by hydrogen atoms. Hydrogen-termination has been used to avoid the boundary effects. We have performed calculations of the

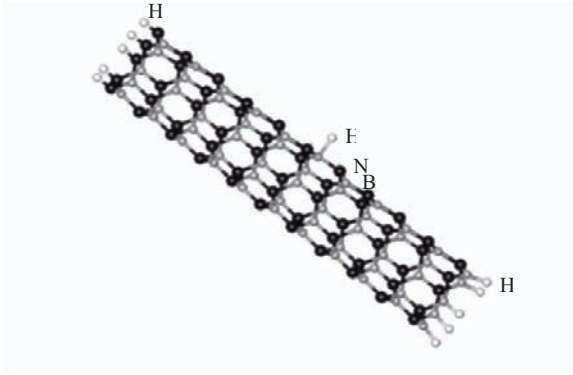


Figure 1. BNNTs (5,0) with hydrogen atom adsorbed on its surface.

quantities relevant to the adsorption on the BNNTs ($n,0$) with $n = 5$ -10. The simulation tube (5,0), shown in Fig. 1, contained 55 boron atoms plus 55 nitrogen atoms in the tube wall and 10 hydrogen atoms at the ends of the tube plus one H atom adsorbed on it. Thus, the smallest tube we have considered is large enough to exclude the boundary effects from the adatom – substrate BNNT interaction at the sites located far from the ends of the tube. This is the more so true for the largest simulation tube (10,0), which contained 240 atoms. The binding of a single H atom to the sidewall of single-walled BNNTs has been studied by placing the H atom on top of N and B sites in the middle of the BNNTs. Adsorption at the centre of the B–N hexagon has not been treated, as it is not expected to be the most active site for the H adatom.

To examine the adsorption properties, we have first optimized the geometric structures of all the clean tubes under consideration. Secondly, for each tube we have found the optimal adsorption distance d_0 between the H atom and the tube. To do this, we have calculated the total energy $E_{\text{tot}}[\text{BNNT} + 2n\text{H}]$ of the hydrogen-terminated BNNTs with the adsorbed H atom on the top of the B or N atom as a function of the distance d between the adatom and the tube. As an example, in

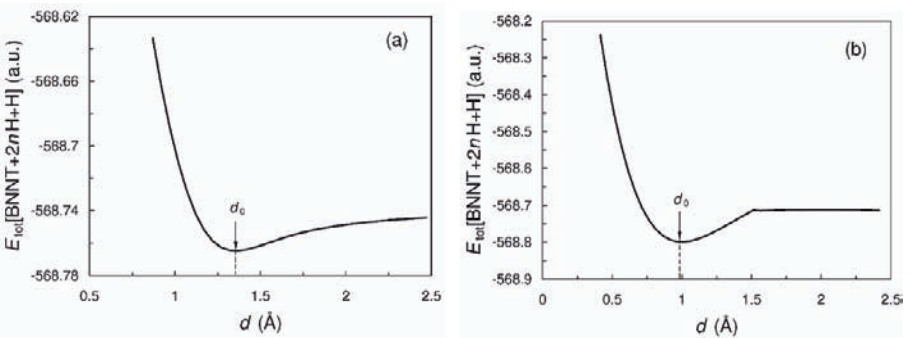


Figure 2. Total energy E_{tot} of the hydrogen-terminated BNNTs (5,0) with the adsorbed H atom on the top of the B atom (a) and on the top of the N atom (b) versus the distance d between the adatom and the tube.

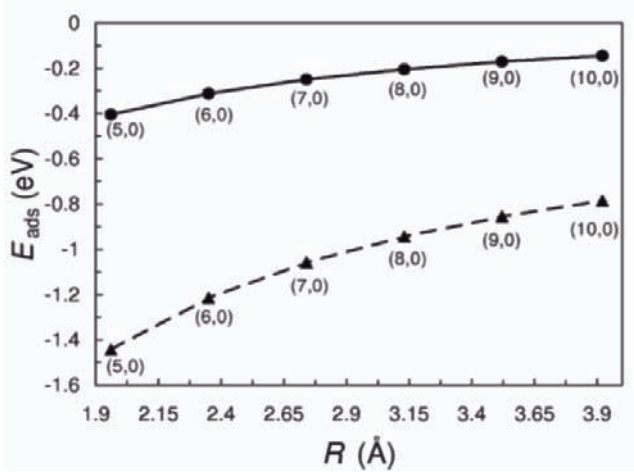


Figure 3. Calculated adsorption energies E_{ads} of a single hydrogen atom on the zigzag BNNTs ($n,0$) with n ranging from 5 to 10 versus the radius R of the tube. The heavy dots and triangles refer to the adsorption on the B atom and the N atom, respectively. The numbers in parenthesis stand for the tube chirality indices. The solid and dashed lines are intended as a guide to the eye.

Fig. 2 we show the result of our calculations for the (5,0) tube, which is typical. The curves in this figure are characterized by the presence of the global energy minimum at the point $d = d_0$. The negative values of $E_{\text{tot}}[\text{BNNT} + 2n\text{H}]$ at this point indicate that the chemical bond between the H atom and the tube is formed. The comparison of the curves in Fig. 2 also shows that the adsorption on the top of the N atom is energetically more favorable than that on the top of the B atom.

The adsorption energy E_{ads} of the H atom on the surface of the BNNT ($n,0$) can be calculated in terms of the above-mentioned total energy $E_{\text{tot}}[\text{BNNT} + 2n\text{H} + \text{H}]$, the total energy $E_{\text{tot}}[\text{BNNT} + 2n\text{H}]$ of the hydrogen-terminated pristine tube and the energy $E_{\text{tot}}[\text{H}]$ of a single free hydrogen atom:

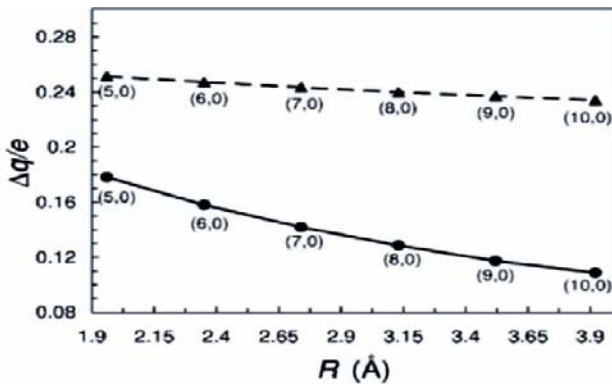


Figure 4. Charge transfer $\Delta q/e$ from the H adatom to the zigzag BNNTs ($n,0$) with $n = 5-10$ as a function of the nanotube radius R . Solid dots and triangles refer to the adsorption on the B atom and the N atom, respectively. The numbers in parenthesis stand for the tube chirality indices. The solid and dashed lines are intended as a guide to the eye.

$$E_{\text{ads}} = E_{\text{tot}}[\text{BNNT} + 2n\text{H} + \text{H}] - E_{\text{tot}}[\text{BNNT} + 2n\text{H}] - E_{\text{tot}}[\text{H}].$$

The results of our calculations of E_{ads} are given in Fig. 3 as a function of the radius R of the tube. As the figure clearly shows, the H atom prefers to be adsorbed on the top of the nitrogen atom. The figure also shows that there is a systematic increase in E_{ads} with increasing R . Thus we have come to a somewhat surprising conclusion that in order to enhance hydrogen storage of BNNTs one should preferably use those with the smallest radii.

We have found that, as the H adatom approaches the surface of BNNT, it acquires a positive charge at the expense of the nearest-neighboring atom of the BNNT. Our calculations show (see Fig. 4) that the charge transfer depends on the bonding sites and the nanotube radius R . The largest charge transfer from the adatom to the nanotube occurs when the H atom is adsorbed on the top of the N atom (in this case its value for the nanotubes considered is about 0.23–0.25 of the electron charge). This is not surprising, since it is well known that nitrogen atoms are more electronegative than boron ones. Thus, we conclude that a single H atom adsorbed on the surface of BNNTs exists substantially in a cationic state.

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INVESTIGATIONS OF THE INFLUENCE OF DIFFERENT ADDITIVES TO THE LANTHANUM RICH MISCHMETAL

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Abstract. The metal hydride electrodes are of a particular interest due to their potential and practical application in batteries. A large number of the hydrogen storage materials have been characterized so far. Nevertheless only selected composite structures were synthesized. This paper deals with the effect of the hydrogen sorption capability and electrochemical characterisation of specific AB₅ alloy composites - AB₅ with SiO₂, B₂O₃, WO₃ and C. The hydrogen storage capacity and kinetics of hydrogen sorption-desorption in the solid phase/gas and solid phase/electrolyte solution systems are presented.

Keywords: hydrogen absorption, composite alloys, metal hydride electrodes, hydrogen spillover

1. Introduction

The best way to attain fast kinetics of the hydrogen electrode reactions is to enhance the intrinsic property of the alloy. Therefore, it is important to define the activities of each of the alloying elements regarding the hydrogen evolution and/or oxidation reaction. To improve the catalytic activity of hydrogen storage materials in alkaline solution, specially selected metal alloys were predicted as additives to the main alloys phase, by taking into account the Brewer-Engel theory of the electronic structure of intermetallic compounds [1-6]. These small additives should be characterized by a higher melting point than the main phase and by an ability to form intermetallic compounds with Ni and Co. Many alloys are reported in scientific publications, but only 2-3 different alloys are used in practical applications as battery electrodes yet [2-6]. It is connected with limited possibilities of individual metals and their alloys in hydrogen activation and storage, as well as with large volume change of crystal lattice during hydrogenation and later pulverization of alloys, what is the one of the weak places of existing metal hydride electrodes. New materials must be found, for example, metal composites with oxides and/or another materials.

An addition of inorganic materials (oxides, for example) to alloy can change hydrogen storage in alloys very much not only to diverse direction. Therefore, if the adsorbed H can be spilled over from hydride alloy to the support and be adsorbed there instead, we should be able to speed up hydrogen storage process considerably. In the case of electrolysis it was demonstrated [7] that Teflon bonded Pt/WO₃ electrodes containing 0.1mg Pt/cm² gave over 400 mA/cm² at 50 mV vs. H₂ at 30°C, compared to less than 40 mA/cm² of Teflon bonded Pt/C electrode containing 1mg Pt/cm². The hydrogen spill over effect was subsequently demonstrated to be operative in H₂ evolution and hydrogenation reactions [8, 9].

For the application purposes, in batteries and battery related fields, hydrogen storage alloys must be characterized by a high hydrogen capacity and moderate hydride stability as well as by an almost constant equilibrium pressure during the solid phase conversion and a low sorption-desorption hysteresis. Usually, PC-isotherms are used to provide the dependence of the equilibrium pressure of hydrogen, $p(H_2)$, on the amount of hydrogen dissolved and/or incorporated in the solid phase at various $T=const$ [6]. There are also some another common criteria for the selection of constituents in a hydride alloy composition, which are based on physical properties of individual elements and their hydrides (electronic structure, atomic bond radius and unit cell volume) – heat of hydride formation, which can be establish as from gas sorption as well as from electrochemical hydrogen sorption methods. Heat of hydride formation (ΔH) is an important parameter characterizing the alloy as a proper hydrogen absorber for various specific applications. Ovshinsky et al. [10] have stated that if the ΔH value ranges between 25 kJ/mol and 50 kJ/mol, the alloy is suitable for battery applications. When it is lower than -15 kJ/mol, then the alloy hydride is not stable enough for charging the MH electrode at room temperature. On the other hand, the alloy hydride is too stable for the room-temperature discharge when the ΔH value exceeds -40 kJ/mol. In the case of composite alloys when hydrogen spillover phenomena will co-exist, complex heat of hydride formation will be the sum from particular heats of hydride formation for alloy and oxide.

The practical energy densities of electrode materials used in energy storage devices are always lower as compared to the theoretical values because finite amounts of binders and conductive particles are necessary to enhance its electrical and mechanical properties. Generally, to characterize the overall electrochemical properties of the metal hydride electrode, all constituents should be taken into account. For example, it is known that nickel and copper, two typical additives for metal hydride electrodes, also form hydrides themselves [11, 12]. Non-sintered electrodes are mostly formed using AB₅-type alloys following next receipt [6]: the hydrogen absorbing alloy particles are mixed with binder (ranging from 0.1 to 7 wt %) and an electrically conductive material (from 0.1 to 4 wt. %) forming a slurry which is then fixed to the current collector (nickel mesh). Sodium, ammonium or potassium poly-acrylates, poly-tetra-fluoro-ethylene (PTFE), poly-vinyl-alcohol (PVA) and carboxyl-methyl cellulose (CMC) are the most used binder materials. The electrically conductive materials usually used are activated carbon, acetylene black, graphite and nickel and/or copper powders.

The common assumption is that the electrochemical performance of metal hydride electrodes is strongly influenced by the additions to hydride forming alloy,

by the type and the amount of the conductive additive, binder and also plastic binder materials. Therefore an object of this research was to test an influence of different additives to lanthanum rich mischmetal (LaMm) alloy AB₅ by using PCT and electrochemical test methods.

The studies on the charge-discharge efficiency of metal hydride electrodes based on LaMm showed that the oxide formation, dissolution of selected elements and the pulverization of an alloy are the three most serious problems in using the hydride electrodes. A simple solution to these problems could be to enrich the grain surface with the catalytically active compounds (platinum black, Ni₃M (M = W, Mo, Mn, V)) or to perform microencapsulation [4-6]. The encapsulation method serves to preserve alloy grains from disintegration due to volume changes occurring during the charge-discharge cycling, and to keep the surface electrochemically active. Electroless coating methods for nickel, copper, duplex nickel is often used to preserve AB₅ alloys. The surface treatment of metal hydride electrodes plays an important role in the performance characteristics -discharge capacity and cyclic life stability. Anyhow, the performance of AB₅ - type metal hydride electrodes needs further improvement; therefore, we used different composite additives to verify the hydrogen absorption kinetics of AB₅ alloys.

2. Experimental

Thermogravimetric (TG) determinations of the sorption characteristics of the La Mm (the cost of mischmetal is much lower than that for La because it is raw material) in comparison to the same metalhydride with different additives were carried out in hydrogen. It was performed in the RISØ National Laboratory, Denmark. Samples have been prepared from AB₅ mixing with WO₃, SiO₂, B₂O₃ or C. The sample pre-treatment was performed as follows: weighting sample on the high precision balance, putting it into TG balance, vacuuming the system, heating up till 260⁰C, cooling down to room temperature, increasing hydrogen pressure to 15 atm, and then vacuuming, the temperature elevating to 40⁰C. Then the experiments were run step by step rising up the hydrogen pressure and waiting until the weight stabilizes to follow with other pressure increase.

Electrochemical Impedance Spectroscopy (EIS) and cyclic voltammetry was used for electrochemical measurements. The impedance and electrochemical parameters were measured using AutoLab PGSTAT 30 (Ecochemie) in the South African Institute of Advanced Material Chemistry of University of Western Cape, South Africa. Different binders were investigated in order to prevent the pulverization of the AB₅ within hydrogenation process. PVA (poly-vinyl-alcohol) and PTFE (poly-tetra-fluoro-ethylene) have been chosen, because they are widely used as binders for metal hydrides. Zeolites are low price and high stability additives and zeolite CVB-400 was selected for our research purposes. It was assumed, that zeolites might be suitable both for hydrogen absorption and as a binder. An alloy sample was pulverized down to 1-20µm of the grain size in several hydriding-dehydriding cycles using different temperatures and pressure of H₂ and ball milling processes. Electrochemical behaviour of alloys was tested in a glass cell with a 6 M KOH solution (the electrolyte resistance was about 0.2 Ohm), using a much larger Pt counter electrode and an Hg/HgO reference electrode. From examined methods the following was considered as the most convenient for

preparing 1 pellet: 1 gram of LaMm powder + 5% additives. To form the pellet pressure of 5 tons to square centimetre for 10 minutes was applied. For PTFA and zeolite additions drying in the vacuum oven was performed for 3.5 hours at 150 and 50⁰C, respectively. For PVA additions the drying in air at 50 ⁰C was used. Before measurements all pellets was immersed into hot alkali solution for several hours to activate them [13, 14].

3. Results and Discussions

Thermogravimetric determinations of the sorption characteristics of the La mischmetal in comparison to the same metalhydride with different additives were carried out in hydrogen. The assumption is that according to the spill-over effect of hydrogen on the oxide surface the uniform forming of the hydrogen bronze (H_xWO_3) will take place. WO_3 is changing colour at the presence of hydrogen atoms from yellow to dark blue and that could be useful indicator that system is absorbing the gas. In the case of the glass phase (SiO_2 , B_2O_3) the spill-over effect on the glass surface will increase the efficiency of the metal hydride forming. In the Figure 1 absolute changes of weight per sample are shown as a function of hydrogen loading time.

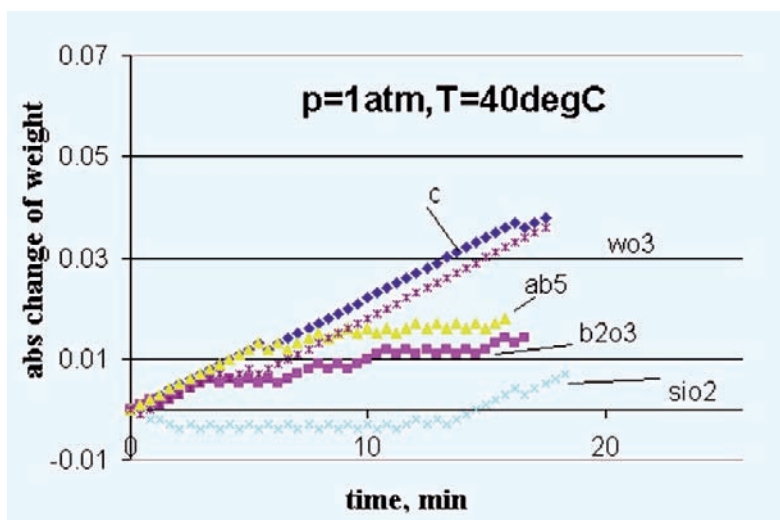


Figure 1. Absolute changes of weight vs. time.

In the case of glass additives slow kinetic was observed during the first 10-15 minutes of exposure to hydrogen. Samples containing B_2O_3 glass and SiO_2 glass absorbed less hydrogen as compared to the LaMm. In the case of C and WO_3 additives, an improved performance was observed after 10 minutes long exposure. Linear increase of the amount of absorbed hydrogen is observed.

In the beginning voltammetric measurements were performed to compare the LaMm only and LaMm with additives. In the Figure 2 is shown that there are no big differences between all additives.

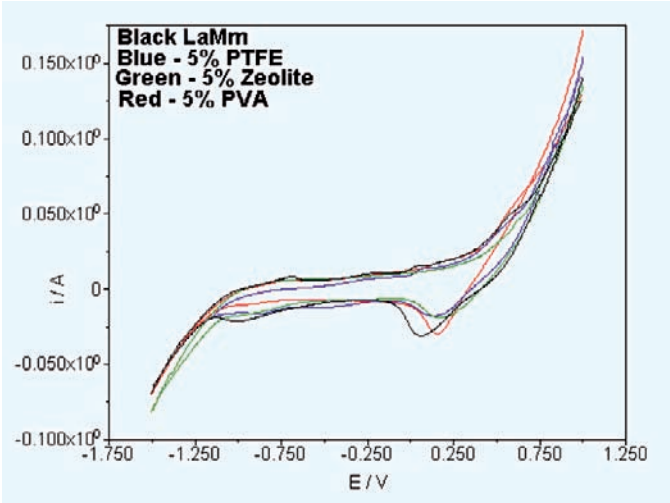


Figure 2. Volt-ampere curves of pure LaMm sample and with additives.

The impedance spectroscopy is most promising for electrochemical in situ characterization. Many papers have been devoted to the AB₅ type MH electrode impedance analysis [15-17]. Prepared pellets with different additives were used for electrochemical measurements and comparing. Experimental data are typically represented by one to three semicircles with a tail at low frequencies. These could be described to the complex structure of the MH electrode, both a chemical structure and porosity [18, 19] and it is also related to the contact between a binder and alloy particles [20]. The author thinks that it is independent from the used electrolyte, the mass of the electrode powder and the preparing procedure of electrode. However, in our case the data accuracy at high frequencies is lower in comparison with the medium frequency region. In the case, the dependence on investigated parameters is small. In Figures 3-5, the electrochemical impedance data are shown as a function of applied potential (1 = -0.35V, 2 = -0.50V and 3 = -0.75V).

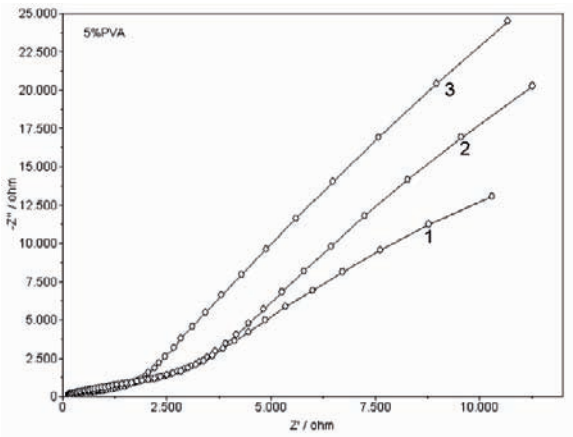


Figure 3. EIS of LaMm + 5% PVA.

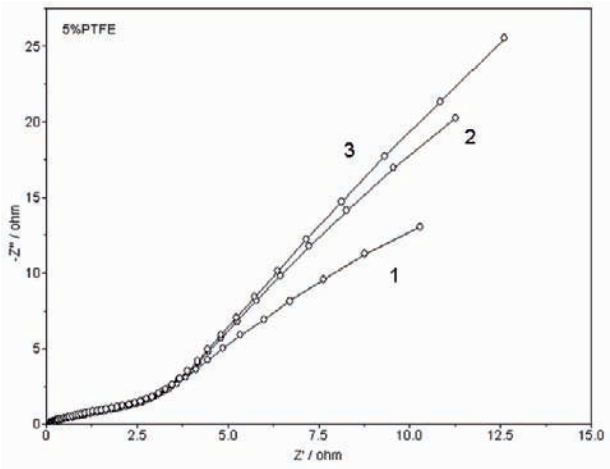


Figure 4. EIS of LaMm + 5% PTFE.

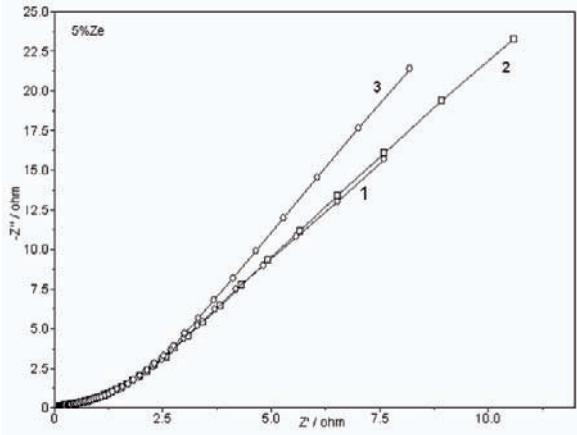


Figure 5. EIS of LaMm + 5% Zeolite.

4. Conclusions

Thermogravimetric studies of LaMm powder with different additives at the temperature 40°C and atmospheric pressure showed low impact of the silica glass phase on the absorption kinetics and absorbed amount of hydrogen. More prolonged milling times must be tested in future. Tungsten oxide and carbon are the most promising additives to Mm so far. The impact of both additives could be explained in terms of spill-over effect, but it is prerequisite for further experiments and convincing proofs.

All applied binders provided pellets with sufficient mechanical stability and similar values of the charge transfer resistance. There will follow experiments with zeolite as possible binder and partly replacement of LaMm in metal hydride

electrodes and larger hydrogen storage apparatus. For future work it is planned to study charge/discharge characteristics and the influence of different binders on electrolytic hydrogen sorption properties.

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ON ELECTROCHEMICAL DEPOSITION OF FULLERENES AND THEIR COMPOUNDS FROM SOLUTIONS

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Abstract. The work demonstrates a principle possibility to produce the films of fullerenes and fullerene-containing products from their solutions by the electrochemical method. Electrical properties of fullerene solutions have been studied. The proposed method can be used for the special-purpose application of fullerene-containing coatings and for synthesis of fullerene compounds with organic and inorganic substances.

Keywords: fullerene, coating, electrochemical properties, microstructure.

1. Introduction

C₆₀ fullerene is a new type of π -acceptors with a number of essential dissimilarities from another acceptor molecules: large size, spherical form, unique electron structure, high symmetry and polarizability. These peculiarities introduce a certain specificity in donor-acceptor interactions in fullerene compounds. Fullerene is a rather weak acceptor. Adiabatic affinity for an electron in the solution is 2.1-2.2 eV [1]. One molecule of C₆₀ fullerene can accept to 12 electrons [1-4] and donate one electron [5], i.e. the charge on a C₆₀ molecule can vary from +1 to -12. Polarizability of a C₆₀ molecule is high ($\alpha \sim 85 \text{ \AA}^3$) and several times greater than that of other π -acceptor molecules. Because of this, polarization Van der Waals forces are of essential importance in the formation of donor-acceptor complexes.

Reversible step transfer of up to 6 electrons per one molecule to form anion radicals is observed in the cathodic polarization of C₆₀ fullerene solutions [6]. Anion particles are stable in aprotic media, however in the general case anion stability decreases with increasing charge [7]. The number of observed steps depends on the medium and experimental conditions. The literature analysis [8-10] has revealed that the use of different solvent systems, base electrolytes and electrodes results in considerable variations in redox potentials for the most extensively studied pairs of C₆₀/C₆₀⁻, C₆₀/C₆₀⁻², C₆₀/C₆₀⁻³.

The electrochemical method is also used for the synthesis of fullerene derivatives, among them C_{60} fullerene salts with alkali metals crystallized at the cathode [11, 12]. No evidence on the electrochemical deposition of fullerenes on the electrodes from organic solvents is available although this method for producing fullerene coatings on metals is of indubitable practical interest.

In the present work the possibility to produce fullerene-containing coatings on the nickel electrodes by the electrochemical method has been studied depending on the chemical composition of a solution and synthesis conditions in particular the cell voltage.

The accepted nomenclature is used in the work. An individual fullerene molecule is referred to as "fullerene". A crystal from fullerene molecules is referred as "fullerite".

2. Experimental

Fullerene electrodeposition has been carried out using a two-electrode cell with 35x10 mm nickel electrodes. The working part of an electrode measures 10x10 mm. A potentiometer is used as the constant-current source. The potentiometer allows the potential difference between electrodes to be varied between 0 and 2000 V and the strength of current to be measured to 1 mA. The working volume of the cell is 30 ml, the electrodes gap is varied in the range from 4 to 6 mm. The fullerene solution in toluene of different concentrations and with the addition of a base electrolyte is used as the working electrolyte. The fullerene has been extracted from the soot produced by the electric arc method. The fullerene contains 84% C_{60} , 14% C_{70} and about 2% higher fullerenes. X-ray phase analysis has revealed that the starting fullerene mixture has the fcc crystal lattice. Experiments have been performed at room temperature, constant current density ($0.9\text{--}0.4\text{ mA}\cdot\text{cm}^{-2}$) or constant electrode voltage. The magnitude of voltage is determined by the electrolyte composition and concentration and can be varied between 5 and 1600 V depending on the experimental conditions. Before experiments the electrodes were polished mechanically with chromium oxide and cleaned with organic solvents.

3. Electrolyte composition and preparation thereof for operation

The working solution for electrochemical studies on fullerenes must assure both good fullerene solubility and sufficient electrical conduction of the solution. Fullerenes dissolve readily in many benzene-type organic solvents including toluene in which fullerene solubility has been much studied. At room temperature the maximum solubility is as much as $2.8\text{ mg}\cdot\text{ml}^{-1}$.

Electrochemical behaviour of fullerenes in solutions depends in part upon the electric properties of the solvent, in this instance toluene. However toluene is an aprotic solvent with a low dielectric constant ($\epsilon \approx 2.7$) resulting in a high electrical resistance of a cell and, consequently, the absence of electrical conduction in the solution. Ethanol has been used as the base electrolyte to ensure electrical conduction in the toluene-fullerene (TF) solution.

Ethanol belongs to the class of polar solvents. Dielectric constant of ethanol is sufficiently high ($\epsilon \approx 24.3$). Ethanol is an amphoteric electrolyte, i.e. it can be both proton acceptor and proton donor. Ethanol mixes readily with toluene, does not

react with fullerene although at high concentrations it is capable of displacing fullerene in hydrocarbon solutions.

Electric conduction of the toluene-fullerene-ethanol (TFE) solution depends upon the electrical properties of ethanol. The volume of ethanol added to the solution has been varied between 10 and 50 vol. % at fullerene concentrations $1.5\div 2.8\text{ mg}\cdot\text{ml}^{-1}$. In this case the operating current density ($0.4\text{--}0.9\text{ mA}\cdot\text{cm}^{-2}$) has been achieved at the potential difference between electrodes from 200 to 1600 V [13]. However a strong electric field between electrodes can produce change in electrical properties of the solution or cause degradation of some of its components.

Additives of the KBr, KOH type have been used for the reduction of the potential difference between electrodes with retention of the same operating current density in the solution. These additives belong to the class of strong electrolytes and are base electrolytes in themselves for ethanol [14]. Concentration of the additives has been chosen in the range from 0.05 to $0.2\text{ mg}\cdot\text{ml}^{-1}$. In this case the potential difference between electrodes has been reduced by 1-2 orders of magnitude at the same operating current density. The volume of ethanol added to the solution has been reduced by 2-5 times, i.e. decreased to 10-15 vol. %.

A special attention has been given to the purification of the working solution components from impurities. Commercial toluene used as the fullerene solvent has been subjected to double purification by distillation. Ethanol for purification from water and some impurities has been subjected to electrolysis within 1-2 h at the operating voltage about 380-400 V. The active additives used in the base electrolyte composition have not been purified additionally because they correspond to the classification as "pure for analysis". The TF solution has been purified from the undissolved particles by filtration using the laboratory filter paper of the "F" make-up.

4. Results and Discussion

The working TFE solution with active additives displays a sufficiently high electrical conduction. This solution has been used in the studies of electrochemical properties of fullerenes and in the electrodeposition of fullerenes as coatings or for the production of a great quantity of product as fullerenes or their compounds on the electrodes.

Figure 1 gives the strength of current as a function of potential difference between electrodes for TE and TFE solutions (curves 1 and 2, respectively). The fullerene concentration in the TFE solution is $2.5\text{ mg}\cdot\text{ml}^{-1}$. The ethanol additive to toluene for both of the solutions is 50 vol. %. Curve 3 (Fig. 1) corresponds to the $I(U)$ dependence for the TFE electrolyte on addition of $0.1\text{ mg}\cdot\text{ml}^{-1}$ KOH, 10 vol. % ethanol and $2.1\text{ mg}\cdot\text{ml}^{-1}$ fullerenes.

As Fig. 1 suggests, the fullerenes presence in the solution somewhat change the volt-ampere characteristic compared to that for the TE solution. The $I(U)$ dependence becomes practically linear in the range of the voltages measured. The value of current strength, all other things being the same, is slightly lower for the TFE electrolyte and higher for the TFE solution with KOH additive compared to that for the TE solution. For the TFE electrolyte with the above mentioned composition and experimental conditions, the total electrical resistance of the cell ($\approx 2.9\cdot 10^5\ \Omega$) has been determined from the $I(U)$ dependence according to Ohm's law for a subcircuit. For the electrolyte with KOH additive, the total resistance

equals $0.7 \cdot 10^5 \Omega$. In the general case electrical resistance of a cell depends heavily both on the electrolyte composition and the concentration of components in the solution.

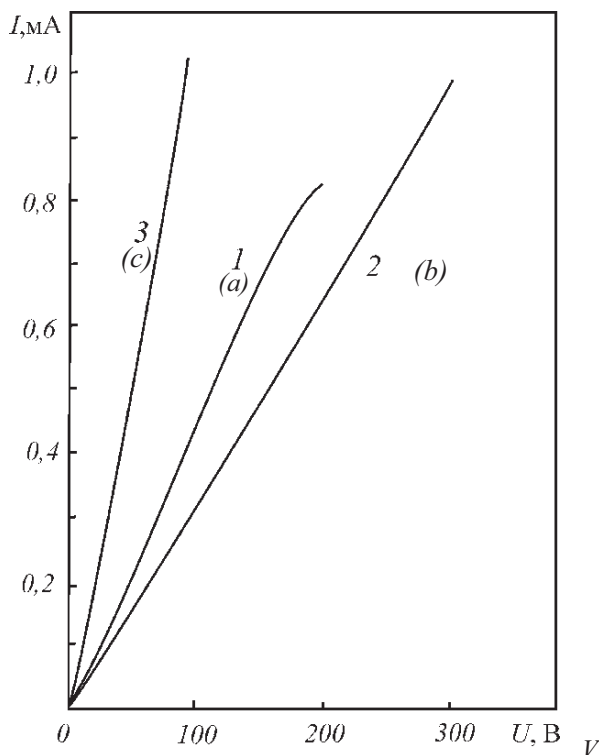


Figure 1. The current strength plotted against the potential difference between electrodes for the different operating solutions: (a) - toluene-ethanol (TE); (b) - toluene-fullerene-ethanol (TFE); (c) - TFE with KOH addition.

An investigation of the time dependence $I(t)$ for the working solutions has revealed the significant decrease in the magnitude of the current (by 20-30%) at the early stage of the experiment (0-30 min), thereafter the value of current strength does not practically change (3-4 hours), then it slowly decreases because of the consumption of reacting components.

The fullerene-containing films have been deposited on the electrodes in electrolysis of the TFE solution. The operating voltage of the cell is 5-80 V for the TFE solution with one of the additives from KOH, NaBr, KBr etc. and equals 200-1600 V for the solution without additives. The films form on the cathode and the anode simultaneously. The 25-100 μm thick films are largely deposited on the anode and the 1-10 μm thick films are deposited on the cathode. The thickness of the films depends on the experiment duration. However the thick films can be produced on the cathode and the thin films can be produced on the anode if the composition of the working solution is varied or the volume proportions of components of the working solution is selected in a certain way. The deposited films are distinct not only in thickness, but also in structure, composition and other

physical and chemical properties. For example, the thick films dissolve readily in toluene and do not dissolve in water while the thin films are not dissolved neither in toluene nor in water.

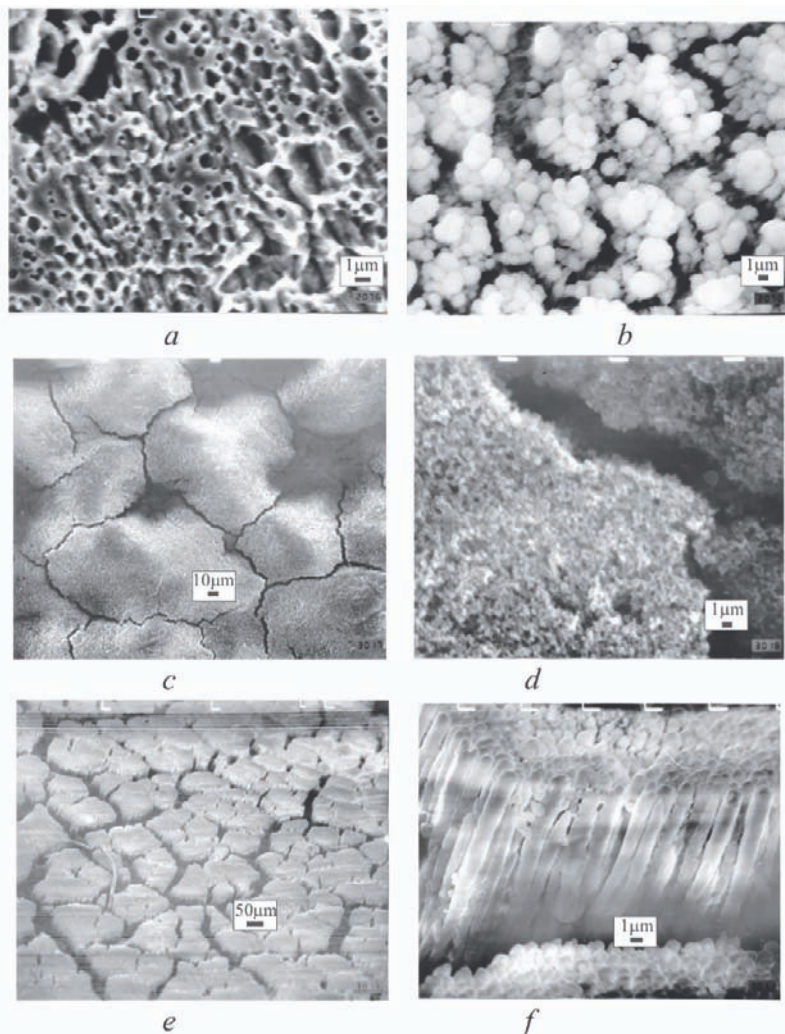


Figure 2. Microstructure of films formed on: (a) the anode without special additions at $U = 200$ V; (b) the cathode without special additions at $U = 200$ V; (c,d) the anode with KOH addition at $U = 40$ V; (e,f) the cathode with KBr addition at $U = 40$ V.

The structures of the thick anodic and cathodic films produced from the working solutions with active additives and without them as well as the structure of the thin anodic film deposited from the TFE solution have been studied using scanning electron microscopy. The thin anodic film produced from the TFE solution without additives (Fig. 2, a) is porous and consists of small crystals. The

cathodic film (Fig. 2, *b*) produced under the same conditions is sponge and consists of spherical particles. The anodic film to 100 μm thick produced from the solution with KOH additive (Fig. 2, *c, d*) consists of small crystals. The cathodic film to 100 μm in thickness produced from the solution with KBr additive (Fig. 2, *e, f*) has a columnar structure. The thick films of fullerites and fullerene-containing compounds produced in one case on the anode and in another case on the cathode have outward resemblance, they are cracked and consist of individual conglomerates $\sim 40 \times 150 \mu\text{m}$ in size. The films crack under drying after washing.

The composition of the anodic and cathodic products formed in electrolysis of TFE solutions have been analyzed using methods of high energy resolution Auger spectroscopy on JAMP-10 and X-ray analysis on DRON-2 instrument in $\text{CuK}\alpha$ radiation according to the standard procedures.

Layer-by-layer Auger spectral analysis of the anodic and cathodic products formed from the TFE solutions has revealed that two groups of spectra show the lines from free carbon (260–280 eV), oxygen (~ 500 eV) characteristic for nickel oxide and nickel itself across the whole thickness of the film (Fig. 3).

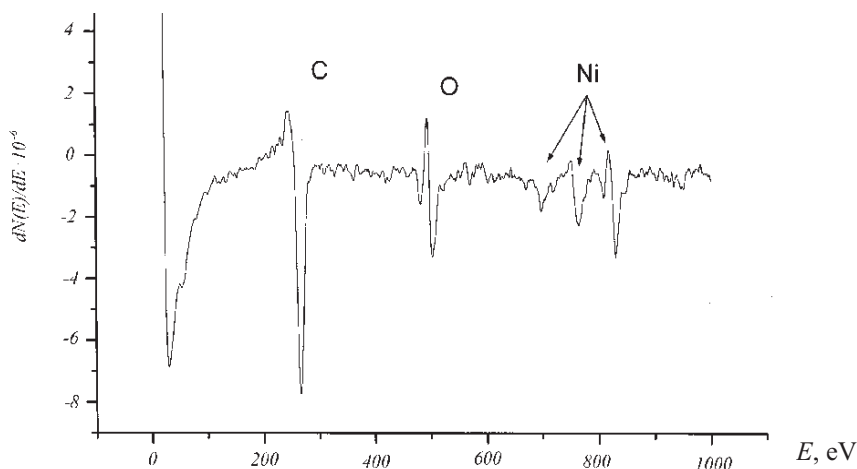


Figure 3. Auger-spectrum of the electrolysis product formed from the TFE solution.

The detailed layer-by-layer analysis of the electrolytic products on both of the electrodes has revealed that the fine structure of carbon spectra changes depending on the depth of Ar ion etching. This may testify that carbon is in different electronic states across the depth of the film, i.e. carbon forms chemical bonds. In analysis of the cathodic product, the change is most evident (Fig. 4, *a, b*) although this may be due to the recharge of carbon atoms under the action of the Ar ion beam in etching.

X-ray studies has been performed on the thick anodic and cathodic films formed in electrolysis of the TFE solution with and without active additives.

Experimental data for the angles of reflection (2θ) and the interplanar spacing (d) obtained from the diffractograms of the electrolysis products under study, and the literature data for these parameters for C_{60} fullerenes with the fcc and hcp



Figure 4. Fragment of Auger-spectrum corresponding to the carbon line. The spectrum was produced for cathodic product of electrolysis: (a) without etching and (b) at the etching with Ar ions over the course of 40 min.

lattices [15] are given in Table 1. According to the X-ray investigations, the diffractograms of the electrolysis anodic product formed from the TFE solution with the active KOH additive have three strong lines of reflection which correspond to the C_{60} fullerite with the fcc lattice (Table 1). Besides the mentioned lines for the C_{60} with the fcc lattice, the diffractograms for the cathodic product formed from the TFE solution have the lines of reflection which correspond to the C_{60} with the hcp lattice (Table 1). These lines are observed on the background of the halo in the range of angles of reflection $2\theta = 14 - 22^\circ$. This halo supposedly corresponds to the non-crystallized part of the fullerite or to the fullerene-organic compounds.

TABLE 1. Experimental and literature data for reflection angles (2θ) and interplanar distances (d) for the electrolysis products and fullerene C_{60}

Electrolysis product	(hkl)	Experimental data		Literature data for C_{60} [15]		Type of lattice
		2θ	$d, \text{\AA}$	2θ	$d, \text{\AA}$	
Anodic (TFE+KOH)	(111)	10,5	8,40	10,8	8,19	fcc
	(220)	17,7	5,01	17,7	5,01	fcc
	(311)	20,7	4,29	20,8	4,28	fcc
Cathodic (TFE)	(100)	10,1	8,75	10,2	8,68	hcp
	(111)	10,6	8,3	10,8	8,19	fcc
	(101)	11,6	7,63	11,5	7,67	hcp
	(102)	14,7	6,02	14,87	5,96	hcp
	(220)	17,6	5,04	17,7	5,01	fcc+hcp
	(311)	20,8	4,28	20,8	4,28	fcc

Figure 5 gives the diffractogram of the thick anodic film electrodeposited from the TFE solution without any additive. The peaks in the diffractogram correspond to the C_{60} fullerene with the fcc lattice.

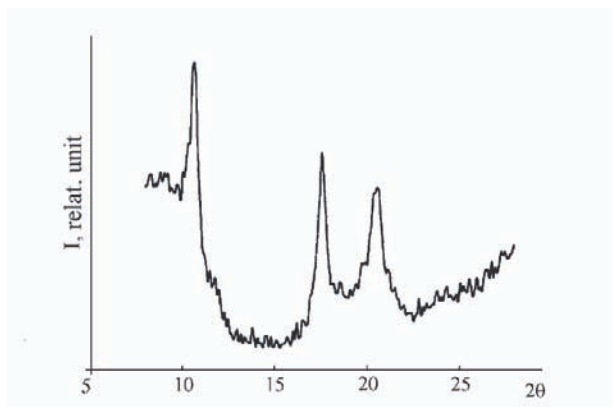
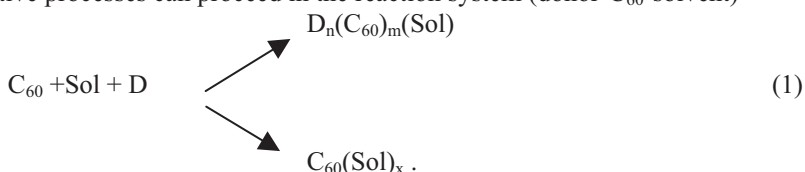


Figure 5. Diffractogram of the thick anodic film electrodeposited from the TFE solution.

5. About the mechanism of electrochemical transformations occurring in electrolysis of the fullerene-containing toluene-ethanol solution with and without active additives

It has been known [6-10] that C_{60} fullerene reacts easily with proton donors and accepts electrons to form anion radicals. Thus, one might expect the preferred fullerene transformations in electrolysis to be related to the fullerene reactions on the cathode. Anion radical transformations can occur both on the surface and in the solution. It has been known that fullerene forms solvates [16] with many solvents (Sol), in particular with toluene. With electrons (D) in the donor medium, two competitive processes can proceed in the reaction system (donor- C_{60} -solvent)



Ethanol can be a donor capable of forming the donor-acceptor compounds with fullerene in the system involved. Donor will displace the solvent from the solvate shell when the ethanol content increases (to 30-50 vol. %) and high excess of the donor relative to the fullerene is obtained.

By analogy with [17] the C_{60}^{n-} anion radicals, which are generated on the cathode under the action of voltage, can reduce the toluene molecules present in the solvate shell. On the other hand, with protons in the medium, protonization of the C_{60}^{n-} anion radicals, which are electrogenerated on the cathode, to hydrofullerenes can proceed in the following reaction



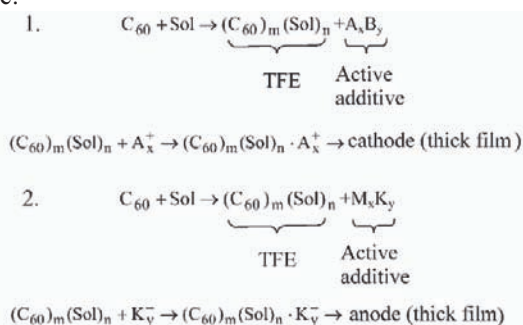
As in the case of water, cathodic reactions of alcohols proceed through the step of hydrogen ion discharge. At all the potentials available in acetonitrile and dimethylformamide, methanol and ethanol do not enter into cathodic reactions [18]. The alcohols are electrochemically inert proton donors in the above solvents.

Data for C_{60} fullerene transformations on the anode are not numerous. Only one irreversible step of oxidation is characteristic of C_{60} fullerene at a potential of

1.28 V [10]. Toluene is oxidized at higher potentials (1.98-2.3 V) [19]. However when the solution contains more readily anode-oxidizable components, such as ethanol and fullerene, oxidation products can react with toluene present in the solvate shell of the combined donor-acceptor complex.

The compounds, which are anodic oxidation products of ethanol and toluene, on the one hand, and oxidation products of the combined solvated donor-acceptor fullerene complex to form the fullerene-containing compound, on the other hand, can form on the anode.

Apparently, the formation of fullerenes and fullerene-containing products on the electrodes in electrolysis of the toluene-ethanol fullerene-containing solution with active additives is connected with the introduction of positively or negatively charged particles from the active additives into the solvate shell of fullerene molecules, and with the electrical transfer of this charged complex followed by its discharge on the electrodes. The process supposedly proceeds according to the following scheme:



However the true pattern of the electrode reactions proceeding in the working solutions is much complicated and invites special investigation.

6. Conclusions

It has been demonstrated that electrochemical deposition of fullerene-containing films from the TFE solutions on the nickel electrodes is possible in principle. It has been found that the thickness, structure, density and chemical composition of the films depend heavily on the type of hydrocarbon solvents for fullerenes, the chemical composition of a base electrolyte and conditions for electrolysis.

The proposed technique can be also used for the synthesis of fullerene compounds with different organic and inorganic substances by the electrochemical method.

Electrodeposited fullerene-containing films can be used as special-purpose coatings and also as intermediate product. Further thermal and thermochemical treatment of such a product will allow the production of the coatings that consist of the product resulted from the interaction of a fullerene-containing film with a substrate. In this case the resulting films will have the chemical composition that goes evenly to carbide (in the case of carbide-forming metal of the substrate) and then to the solid solution of carbon in the substrate. Such a surface will exhibit the tribological properties of fullerene and hardness of carbide and retain the unique chemical composition of the coating.

Hence the proposed method is very promising both for the synthesis of fullerene-containing products and for the surface treatment of finished products with the aim of giving them the unique properties.

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NOVEL CARBON NANOSTRUCTURES PRODUCED BY ELECTROCHEMICAL METHOD

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Abstract. The paper presents results of theoretical and experimental investigations of the process of electrochemical conversion of organic dielectrics into nanosized carbon structures. A new low-temperature method for the synthesis of fractal carbon materials with micro- and nanoparticles having a fibrous, spheroidal, dendritic, and other structure has been briefly characterized.

Keywords: non-graphitic carbon; electrochemical treatment; mass-spectroscopy

1. Introduction

The processes of transformation of organic compounds into new allotropic forms of carbon generally involve the stages of destruction of molecules, release of carbon in free atomic state, and subsequent, often spontaneous, formation of structures organized in a new fashion in three-dimensional space. This way is undoubtedly very fruitful, is widely used on industrial scale, and basically new technological approaches may be expected in this field in future. It appears to us, however, that the capabilities of milder low-energy synthesis have been tested not to the full as yet. In particular, a method for the formation of carbon nanostructures in the valve metal subsurface layer by the action of electric current on aromatic hydrocarbons in the presence of an electrolyte at room temperature has been developed by us and patented. The choice of arenes as original reactants is very expedient since they belong to fairly good solvents for fullerene-like clusters; this makes it possible to analyse reaction semiproducts *in situ*.

2. Experimental

A characteristic feature of the carbon modifications obtained by the method developed by us is their fractal structure (Fig. 1), which manifests itself by various geometric forms. In the electrochemical cell used by us, the initiation of the benzene dehydrogenation and polycondensation process is associated with the occurrence of short local discharges at the metal electrode surface. Further development of the chain process may take place spontaneously or accompanied with individual discharges of different duration and intensity, or in arc breakdown mode. The conduction channels that appear in the dielectric medium may be due to the formation of various percolation carbon clusters.

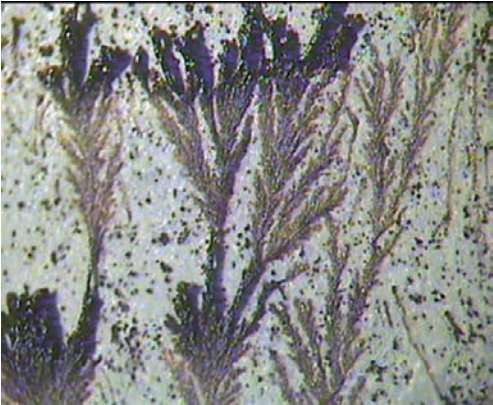
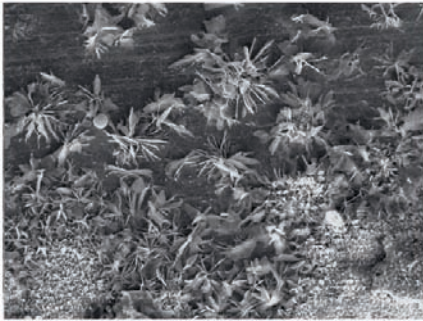
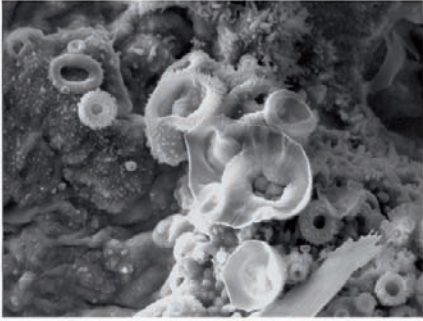


Figure 1. Appearance of the fractal carbon structures obtained. Magnification X10.

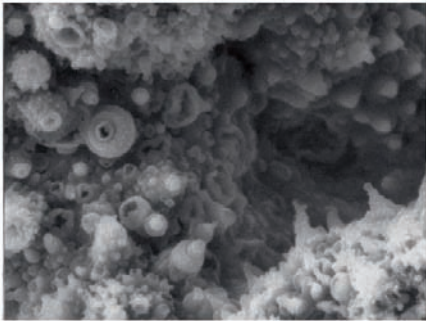
Electron microscope investigations (“Tesla”) showed that depending on experimental conditions, several carbon structure types are produced, which are sufficiently often reproduced for them to be identified as typical morphological forms [1].



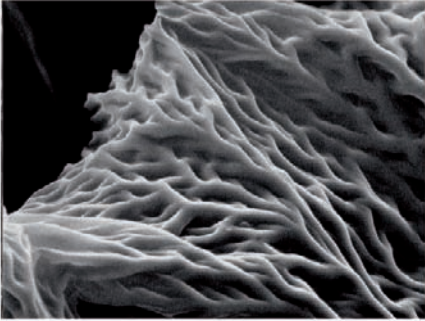
a



b



c



d

Figure 2. Electron micrographs of carbon structures obtained under different conditions.

As is seen from the micrographs, in the carbon structures there are multiple branched fibers, which consist of finer subfibers (Fig. 2 *d*), sheaf-like bundles of particles, spherical, tubular and conical elements (Fig. 2 *a, b, c*).

To determine the chemical composition of the above structures, X-ray photoelectron spectroscopy ("Kratos" Anal. Series 800) was employed. In X-ray photoelectron spectra we found the principal line of C1s electron with a bond energy of 284 eV (80 %) and two peaks at 285.45 and 287.2 eV on decomposition of the broadened portion of the spectrum, which is close in values to the C-C and C-H bond energies.

Similar processes for producing conducting polymeric films of benzene and its derivatives had been studied earlier [2-4]. Necessary conditions for the successful realization of these processes are the use of a platinum electrode and a polar solvent in the presence of catalysts (Lewis acids) and thermostating of the reactor at -75°C . A poly(para)phenylene polymerizate of the linear structure $\text{H}-(\text{C}_6\text{H}_4)_n\text{H}$ with the degree of polymerization n , which varies between 3 and 16, is formed. Forced convection of monomeric molecules facilitates the polymerization reaction in the diffusion layer near the electrode and the formation of a dense film on the electrode surface and prevents the formation of poly(para)phenylene in the bulk.

In contrast to the above processes, the method developed by us is aimed at the creation of branched polyphenylene chains, the development of which, which is due to electron and proton transfer, takes place in accordance with field lines. In this case, favorable conditions for the formation and stabilization of polycyclic carbon clusters of different geometrical structure are created in local spaces of the reaction medium. We suppose that the process occurs according to the following scheme. At the first stage of spark discharge, a relatively narrow cylindrical conduction channel appears in the dielectric liquid; this channel is filled with a heated substance, in which the ions and electrons move in the opposite directions. A current flows along the conduction channel, and at its boundaries is formed a coaxially oriented carbon film, which is insoluble in benzene. The thickness and length of the film can be changed by varying the experimental conditions. In this way hollow and filled carbon fibers and, in ideal case, monolayer nanotubes of predetermined length are produced.

The second discharge stage is the formation near the conduction channel of a gas bubble from the vapor of the liquid, which expands owing to high pressure. The boundary of the conduction channel moves at a high speed in the radial direction, forming a pressure front, in which the pressure changes abruptly from the initial value (in the bulk of benzene) to a high value near the outer bubble boundary. If one manages to achieve a sufficiently intensive hydrogen withdrawal, spherical carbon structures are formed during polycondensation.

The third discharge stage is accompanied by current stoppage, separation of shock wave from the gas bubble and continuation of its expansion by its own momentum. The shock wave is suppressed by the surrounding liquid, and the pressure inside the bubble falls abruptly. Carbon structures take under such conditions the shape of a tore, truncated sphere, etc.

In real systems the formation of thermodynamically stable carbon structures having the minimum surface energy is inevitably accompanied by the separation of the elements that are excessive for some reasons due to chain breakage, energetic or steric misfit, etc. Besides, semiproducts that are readily soluble in benzene enter

the reaction space. In this case, polar compounds are concentrated on the electrode surface or transfer into the electrolyte, and non-polar molecules and clusters are arranged in the non-polar solvent. This allowed us to form a conception of characteristic elements, which may be classified as precursors of synthesized carbon materials.

Using field mass-spectrometry, the composition of the reaction products dissolved in benzene and substances that are desorbed from carbon materials in the case of field ionization under temperature gradient conditions has been analysed. According to the experimental conditions, a sample was applied to a needle-shaped gold emitter, evacuated, thermostatted at 20°C and ionized at a total field intensity of 10^7 - 10^8 V/cm.

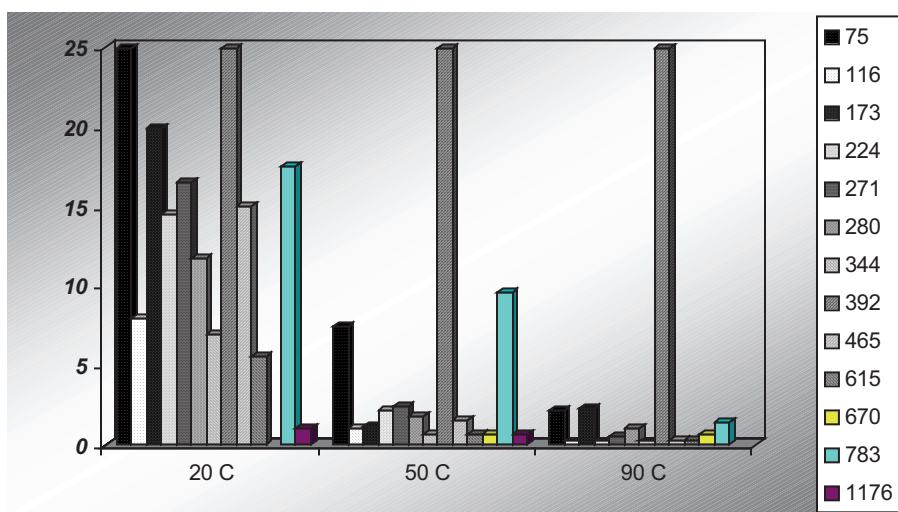


Figure 3. Composition of a benzene solution of carbon compounds according to the results of a mass-spectrometric analysis. On the y axis are peak intensities in mass-spectra, on the x axis are temperature values. In the table are given the mass numbers of the peaks (m/z).

Figure 3 shows a histogram which depicts field desorption mass-spectra of a benzene solution of protoparticles formed on benzene polycondensation [5]. Thirteen main peaks were noted. Sample temperature: 20, 50, 90 °C. It can be seen that the composition and the ratio of the constituents vary with rising temperature, i.e. carbon-containing compounds and associates are partly destroyed by desorption. In this case, certain regularities are observed. For instance, the high m/z values are divisible by some low m/z values or can be made up from several lower m/z values, for example:

$$m/z \ 783 \cong 2 \times m/z \ 392,$$

$$m/z \ 1176 \cong 3 \times m/z \ 392,$$

$$m/z \ 670 \cong m/z \ 392 + 280,$$

$$m/z \ 615 = m/z \ 344 + 271 \text{ etc.}$$

Proceeding from peak intensity values, one can distinguish the main molecular ions. For example, the predominant fragment is the substance with a molecular mass of 392 AU. On the basis of mass values, the presence in the mixture of indene C_9H_8 , diphenylnaphthalene $C_{22}H_{16}$, cation-radicals of triphenylene $C_{18}H_{12}$, benzfluoranthene $C_{18}H_{10}$, tetra(peri-naphthylene)anthracene $C_{54}H_{26}$, and other polycyclic hydrocarbons with five- and six-membered rings in the molecule may be assumed.

The model, proposed by us, of such a molecule with the molecular formula $C_{32}H_8$ is a rather rigid structure (Fig. 4), in which six-membered rings form a three-dimensional quasi-cylindrical tube [6].

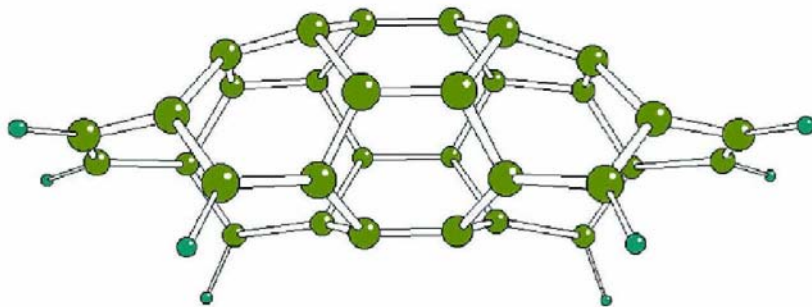


Figure 3. Model of the hydrocarbon molecule $C_{32}H_8$ of 392 amu mass.

Such a molecule can be stabilized by a system of delocalized π -electrons, which is closed into a toroid of 10 aromatic rings. Reactive sites are four CH groups, which are at the ends of this molecular tube. Such substances belong apparently to a new class of organic compounds, which is intermediate between planar polycyclic aromatic hydrocarbons and three-dimensional fullerenes, nanotubes. Quantum-chemical calculations of the electronic and spatial structure of $C_{32}H_8$ and some other molecules indicate that they have an increased reactivity and semiconductor properties.

3. Conclusion

The results given indicate the electrochemical method for the synthesis of nanostructured carbon materials to be promising. In the reaction space, dissipative self-assembly of carbon compounds takes place by the action of electric discharges. In this case, structures of new type can be formed, which are transitional between polycyclic aromatic hydrocarbons and fullerenes, nanotubes.

Acknowledgements

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STRUCTURE OF SOLID AMORPHOUS PHASES OF WATER AND CAPTURE OF MOLECULES CH₄, H₂ IN MULTISTRUCTURES OF ICE

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Abstract. It is suggested that high density amorphous (HDA) and low density amorphous (LDA) phases of ice can be of interest for creation on their basis of adjustable stores hydrogen fuel in the form of CH₄. A nanostructure of these cryogenic phases of water, mechanisms of their polyamorphic transformations, properties to accumulate methane and hydrogen are studied. New model of cryogenic amorphous glasses of water and computer modeling transport of methane and hydrogen molecules inside cellular nanostructures of HDA and LDA are developed within the limits of fundamental theoretical concepts thermo field dynamics and quantum-field chemistry. It is proved that the energetic barrier (6 kJ/mol) of hydrogen mobility is much more lowly then in case of methane (132 kJ/mol). Molecules of methane are strong confined inside supermolecules (H₂O)_n. As have shown essential distinction in the average sizes of compact supermolecules (H₂O)_n in a cryogenic HDA-ice ($n \sim 10^5$) and LDA-ice ($n \sim 30$) allows to change a share of methane accumulation inside of supermolecules of amorphous ice. In HDA-ice large supermolecules can accumulate a lot more methane molecules then in case of LDA-ice. In principle, density jumps on polyamorphic transition of ice allows to obtain reversible accumulation of methane inside cellular nanostructures of cryogenic amorphous ice. It is important that the degree of accumulation can be sharp adjusted by pressure and temperature.

Keywords: hydrogen accumulator, hydrated methane, polymorphism, phase transition, nanostructure of ice, modeling

1. Introduction

Well-known that there is striking polyamorphism of ice having two very different cryogenic amorphous phases [1-4]. Under normal conditions water is a liquid, but glassy water – also called amorphous ice – can exist when the temperature drops below the glass transition temperature T_g (about 130 K at 1 bar). Although glassy water is a solid, its structure exhibits a disordered liquid-like arrangement. Low-density amorphous (LDA) ice has been known to exist for 60 years, and a second kind of amorphous ice, high-density amorphous (HDA) ice, was discovered in 1984 [1-3]. Polyamorphic transition of ice is accompanied by a surprisingly sharp and surprisingly large volume change – more than 20% – when thermodynamic parameters such as temperature or pressure change infinitesimally [4].

These amorphous phases of ice can be of interest for creation on their basis of adjustable stores hydrogen fuel in the form of methane and other. Progress in understanding nature of ice amorphism has been made using developments of fine experiments. But data about formation hydrate methane in amorphous ice are scarce. For quite some time now the scientists have not been trying to identify ways to resolve this problem by studying different samples of ice and learning what combinations of pressure and temperature keep the methane locked up. Other party to problem is how the methane can be extracted.

In a given work computer simulations devoted to study of nanostructure of abovementioned cryogenic amorphous phases of ice, mechanisms of their transformations, and properties to accumulate methane and hydrogen was realized within the theoretical concepts thermo field dynamics [5] and quantum-field chemistry [6-9]. We developed two models of nanostructures corresponding to HDA-ice and LDA-ice, respectively. Some computations of energetic barriers locking molecules CH_4 and H_2 inside of amorphous ice were fulfilled.

2. Modeling of polyamorphic transition in ice

Our approach based on experimental fact that in conditions enough fast cooling at $T < 133\text{K}$ water is able to form amorphous phases [1-4]. There is polyamorphism of ice, but for all that ice has only two essentially different amorphous forms. In the field of low pressure the amorphous phase of low density is formed, and at increase of pressure there is an amorphous phase of higher density. Qualitative scheme of this polyamorphic transition in ice is shown on Fig. 1. At change of pressure or temperatures in amorphous phases occur more then 20% jumps of density.

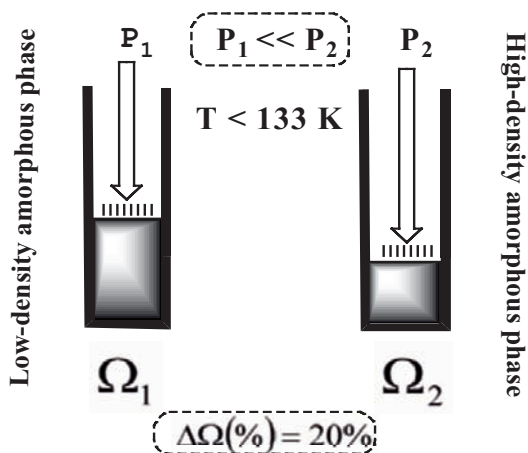


Figure 1. Low-density amorphous (LDA) ice and high-density amorphous (HDA) ice.

With the purpose of explanation of such kind polyamorphic transition in ice we suggest to take under consideration some nanostructural models of cryogenic amorphous glasses of water within fundamental approaches thermo field dynamics [5] and quantum field chemistry [6-9]. According to these theories the condensed

phases of water is a compound nanosystem of water supermolecules $(\text{H}_2\text{O})_n$, displayed on Fig. 2. The internal structure of supermolecule is defined by some spatial grid of intramolecular hydrogen (O—H—O) α -bonds, which form a cellular structure. Ring fragments (O_6H_6) form most penetrable walls of this cellular structure. Aqua nanoparticles interact with each other by means of two kinds of intermolecular bonds: exchange hydrogen (O—H...O) β -bonds and no-exchange electrostatic γ -bonds [7].

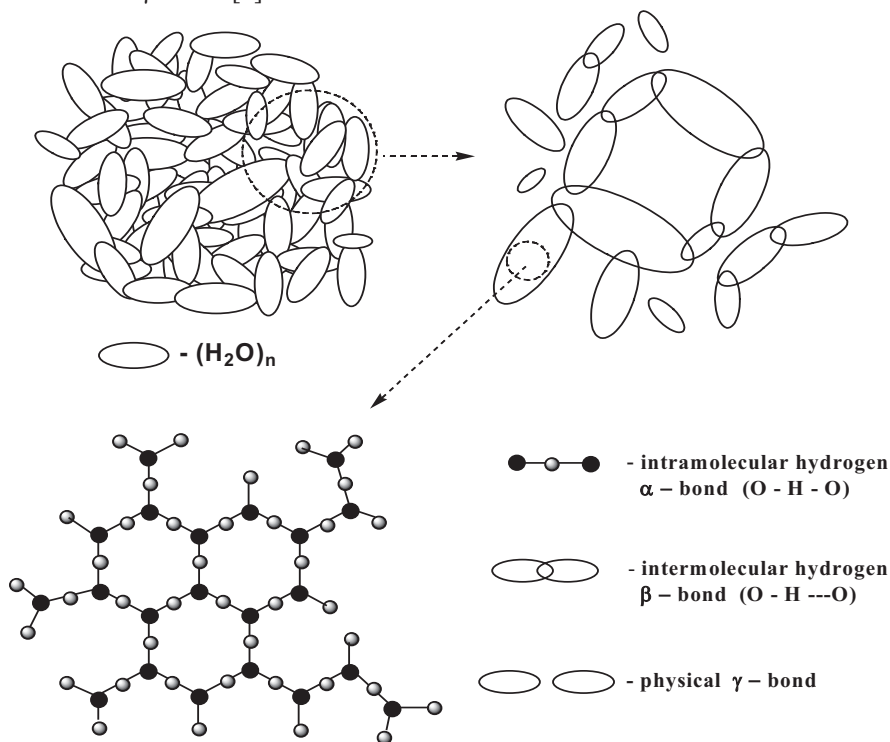


Figure 2. Structure of the condensed phases of water in quantum-field chemistry.

Fluctuate rearranging topological structure of (α, β, γ) -bonds defines transformation of various phases of water. Share distribution of quantity hydrogen α -bonds, hydrogen β - bonds, and electrostatic γ -bonds of supermolecules $(\text{H}_2\text{O})_n$ determines a nanostructure of the condensed phases of water. Within the limits of thermo field dynamics share distributions of three types of bonds are received by methods of statistical thermodynamics. For finding of metastable share distribution of bonds we use a minimization of Gibbs energy having the next standard form:

$$G(\alpha, \beta, \gamma) = U(\alpha, \beta, \gamma) - \tau \sigma(\alpha, \beta, \gamma) + p \Omega(\alpha, \beta, \gamma). \quad (1)$$

Here $U(\alpha, \beta, \gamma)$ – internal energy, $\sigma(\alpha, \beta, \gamma)$ – entropy, $\Omega(\alpha, \beta, \gamma)$ – volume of a system, and p – pressure, τ – temperature of a thermostat. Notice that $\tau = \kappa T$, $S = \kappa \sigma$, where κ is constant by Boltzman.

Procedure of minimization is restricted by balance Equation, as follows:

$$d\alpha + d\beta + d\gamma = dn; \quad (2)$$

where α , β , γ – denote quantity of corresponding types of bonds, and n is the total of bonds.

In pair interaction approach the internal energy has a form:

$$U(\alpha, \beta, \gamma) = N_{H_2O} \varepsilon_{H_2O} + \alpha \varepsilon_\alpha + \beta \varepsilon_\beta + \gamma \varepsilon_\gamma; \quad (3)$$

where ε_{H_2O} is an energy of a single molecule H_2O , and ε_α , ε_β , ε_γ denote energies of corresponding types of bonds of the molecule with its environment.

For ideal solutions an expression of entropy has next standard form:

$$\sigma(\alpha, \beta, \gamma) = \ln \frac{n!}{\alpha! \beta! \gamma!}; \quad (4)$$

and the volume of phase of water is presented in an additive kind, as follows:

$$\Omega(\alpha, \beta, \gamma) = N_{H_2O} \Omega_{H_2O} + \alpha \Omega_\alpha + \beta \Omega_\beta + \gamma \Omega_\gamma. \quad (5)$$

In Eq. 5 Ω_{H_2O} denotes a volume of confined molecule H_2O , and volumes Ω_α , Ω_β , Ω_γ represent some effective topologic volumes of corresponding types of bonds, which are given by next expressions:

$$\Omega_\alpha = \frac{4}{3} \pi \left(\frac{R_\alpha}{2} \right)^3, \Omega_\beta = \frac{4}{3} \pi \left(\frac{R_\beta}{2} \right)^3, \Omega_\gamma = \frac{4}{3} \pi \left(\frac{R_\gamma}{2} \right)^3. \text{ Here } R_\alpha, R_\beta, R_\gamma$$

denote equilibrium bond lengths of proper types of bond.

Applying approximate formula $\ln x! \approx x \ln x - x$ one can obtain share sizes, as follows:

$$v_\alpha = \frac{1}{1 + e^{\frac{(E_\alpha - E_\beta) + p(V_\alpha - V_\beta)}{RT}} + e^{\frac{(E_\alpha - E_\gamma) + p(V_\alpha - V_\gamma)}{RT}}},$$

$$v_\beta = \frac{1}{1 + e^{\frac{(E_\beta - E_\alpha) + p(V_\beta - V_\alpha)}{RT}} + e^{\frac{(E_\beta - E_\gamma) + p(V_\beta - V_\gamma)}{RT}}},$$

$$V_\gamma = \frac{1}{1 + e^{\frac{(E_\gamma - E_\alpha) + p(V_\gamma - V_\alpha)}{RT}} + e^{\frac{(E_\gamma - E_\beta) + p(V_\gamma - V_\beta)}{RT}}} \quad (6)$$

Here $V_\alpha = N_A \Omega_\alpha$, $V_\beta = N_A \Omega_\beta$, $V_\gamma = N_A \Omega_\gamma$ are molar volumes of corresponding types of bond.

In particular for cryogenic amorphous phase of ice share of physical intermolecular χ -bonds is negligible component. In such case formulas for equilibrium share sizes come to expressions:

$$V_\alpha = \frac{1}{1 + e^{\frac{(E_\alpha - E_\beta) + p(V_\alpha - V_\beta)}{RT}}}, V_\beta = \frac{1}{1 + e^{\frac{(E_\beta - E_\alpha) + p(V_\beta - V_\alpha)}{RT}}}. \quad (7)$$

In amorphous ice computing energies of α -bonds and the β - bonds average: $\varepsilon_\alpha \sim -32$ kJ/mol, and $\varepsilon_\beta \sim -26$ kJ/mol, accordingly. Equilibrium share distribution of hydrogen α -bonds and β - bonds in HDA ice at cryogenic temperature $T = 133$ K and high-pressure $P = 5 \cdot 10^8$ Pa average: $v_\alpha = 99,47\%$, $v_\beta = 0,53\%$. Increasing of temperature up to $T = 273$ K and dropping pressure $P = 10^5$ Pa increase share of β -bonds sharply: $v_\alpha = 91,8\%$, $v_\beta = 8,2\%$. This distribution corresponds to LDA-ice. Taking these share distributions and calculated average equilibrium bond lengths $R_\alpha \approx 1,8$ Å, $R_\beta \approx 2,6$ Å it is possible to estimate average sizes L_n of supermolecules $(H_2O)_n$ in HDA-ice and LDA-ice by using next expression:

$$L = \frac{R_\alpha^3 v_\alpha}{R_\beta^2 v_\beta}. \quad (8)$$

As a result one obtains that average size of compact supermolecules $(H_2O)_n$ in a cryogenic HDA-ice is equal to 18 nanometers that corresponds to $n \sim 10^5$ molecules of water. The same as liquid water under normal conditions LDA-ice has an average size of compact supermolecules $(H_2O)_n$ about 1 nanometer that corresponds approximately $n \sim 30$ molecules of water. These distinctions at a size of compact multiparticles can serve for explain observable density jump at polyamorphic transition of ice. According to scheme of this transition shown on Fig. 3 one comes to think of it. Indeed, knowing share distributions of amorphous phases it is possible to calculate percentage change of volume:

$$\omega(\%) = \frac{\Omega_1 - \Omega_2}{\Omega_1} \cdot 100\% = \left(1 - \frac{\Omega_2}{\Omega_1}\right) \cdot 100\%; \quad (9)$$

where $\Omega_1 = \nu_\alpha^1 \Omega_\alpha + \nu_\beta^1 \Omega_\beta$ and $\Omega_2 = \nu_\alpha^2 \Omega_\alpha + \nu_\beta^2 \Omega_\beta$. Substituting previous calculated values, one takes $\omega(\%) = 15,1\%$ that is in a good agreement with experimental data.

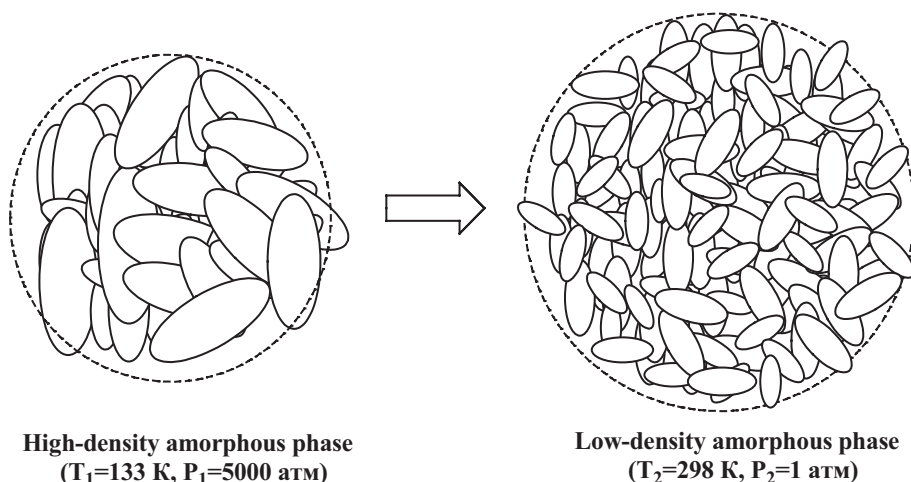


Figure 3. Nanostructural model of polyamorphic HDA $\rightarrow$ LDA transition of ice.

3. Computing of energetic barriers locking CH_4 and H_2 in amorphous ice

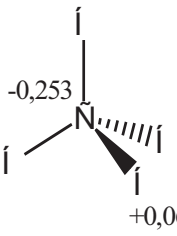
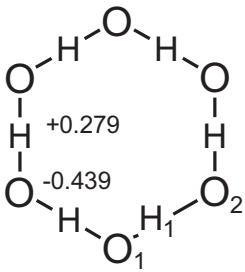
Quantum-field chemistry concept [5-9] treat transport of molecules inside the condensed phases of water as conduction through emptiness of two kinds (see Fig. 2). It is intramolecular emptiness restricted by grid intramolecular hydrogen ($\text{O}-\text{H}-\text{O}$) α -bonds inside supermolecule and, secondly, it is supramolecular emptiness lying between supermolecules confined by network of supramolecular hydrogen ($\text{O}-\text{H}\dots\text{O}$) β -bonds and electrostatic γ -bonds.

Let us taking under consideration computing of energetic barriers that lock transport methane and hydrogen molecules inside of cellular nanostructure of supermolecule. It is well known that ring fragments (O_6H_6) form most penetrable walls of water cells. This stable ring of opposite charges has about 0,6 nm across diameter. Transport of any molecules through cellular grids has as the basic limiting stage overcoming the most penetrating barriers that lay in a direction of an axis of a ring wall (O_6H_6) of water cell. Therefore it is needed to investigate transport of molecules CH_4 and H_2 through barriers laying in this direction only. Forces of intermolecular adhesion operate between walls of a cell of water and molecules of fuel. Potential energy of adhesive chemical ($\text{O}-\text{H}\dots\text{O}$) β -bond and physical γ -bond was calculated by density functional method developed in the frame of quantum field chemistry concept [5].

Necessary data about spatial distributions of electron charge density inside molecules had been taken from calculations by using of standard molecular orbital

method in the minimal basis set (STO-3G). Results of calculations are shown in Table 1.

TABLE 1. Calculated parameters of methane, hydrogen and supermolecular ring(O_6H_6)of ice

Molecular system	Parameter	Value
$H-H$	$L(H-H), \text{\AA}$	0.99
	$L(C-H), \text{\AA}$	0.98
	$L(H-H), \text{\AA}$	1.16
	$\alpha(H-C-H), \text{degrees}$	107.5
	$L(O_1-H_1), \text{\AA}$	1.03
	$L(O_2-H_1), \text{\AA}$	1.80
	$\alpha(H-O_1-H_1), \text{degrees}$	117.9
	$\alpha(O_1-H_1-O_2), \text{degrees}$	177.8

Calculated potential curves of energetic barriers locking transport CH_4 and H_2 through a ring (O_6H_6) are shown on Figs. 4, 5. In case of methane carrying through the cyclic fragment the barrier is very high (132 kJ/mol). On the contrary, the barrier for transport of hydrogen molecule is much small (6 kJ/mol). In case of methane the high barrier is mainly connected with forces of pushing away of its three-dimensional arraying hydrogen atoms from the ring at attempt to pass through it. In the second case the barrier of repulsion is weak because of the big remoteness between atoms of hydrogen and any atoms of the ring.

Therefore in the developed model of specific cellular nanostructure of the amorphous ice quantum mechanism of confinement determines reliable blockage of methane molecules. It is obvious that there is not sufficient blockage of track conductivity for hydrogen molecules in the amorphous ice. This channel operates as a result of track moving of single H_2 through ring "windows" (O_6H_6) of cellular nanostructure of the condensed state of water.

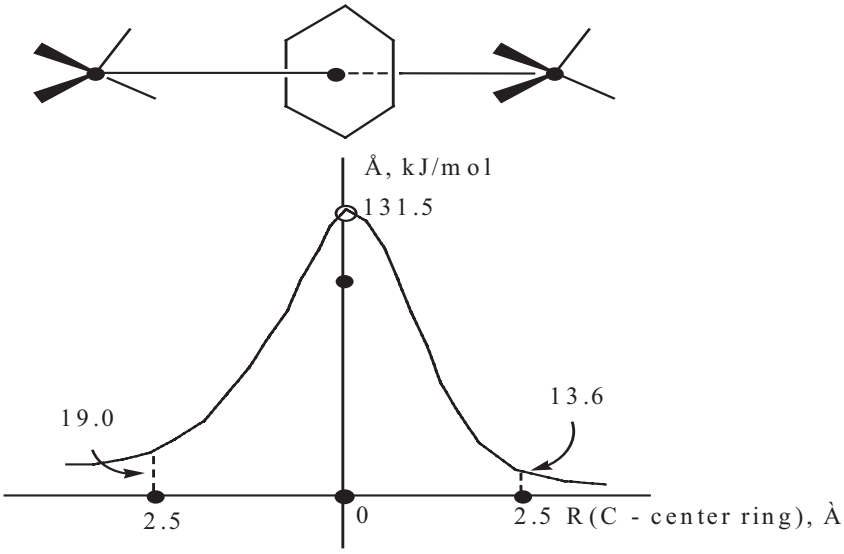


Figure 4. Potential curves of transport CH_4 through a ring (O_6H_6).

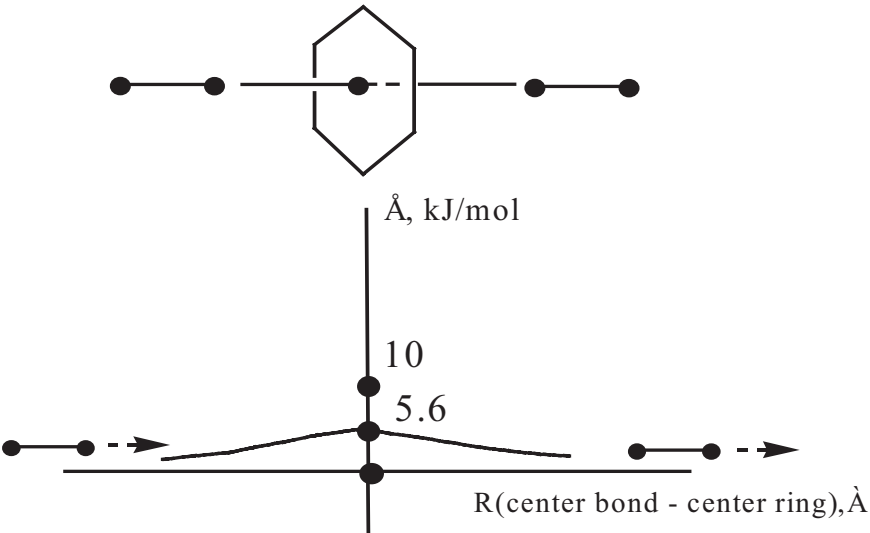


Figure 5. Potential curves of transport H_2 through a ring (O_6H_6).

5. Conclusions

In conclusion of this communication some applications of obtained results to substantiation possibilities to use ice polyamorphism phenomena for adjustable stores hydrogen fuel in the form of CH_4 are discussed.

The energetic barrier for carrying of hydrogen molecule through cellular multistructure of the amorphous ice is essentially less than analogical transport barriers for methane. In agreement with experiments it causes the effective mechanism transportation of hydrogen molecules in the condensed state of water. Methane mobility inside multistructures of amorphous ice is very small, as they are locked inside of cells of water $(\text{H}_2\text{O})_n$. Therefore it is probably to expect that amorphous phases of an ice can be of interest for creation on their basis of stores CH_4 . And what is more, as have shown our calculations essential distinction in the average sizes of compact supermolecules $(\text{H}_2\text{O})_n$ in a cryogenic HDA-ice ($n \sim 10^5$) and LDA-ice ($n \sim 30$) allows to change a share of accumulation of methane inside of supermolecules of water. In HDA-ice molecules of water collected in set of large nanoparticles can accumulate a lot more methane molecules then in case of LDA-ice.

Notice that transformation from a crystalline phase to presumably metastable amorphous phases is called amorphization. It is very promising to use for making of adjustable stores hydrogen fuel phenomena that is called polyamorphism. This term meaning that the pure material can exist in more than one amorphous state. In principle, the abovementioned mechanism of density jumps at polyamorphic transition of ice allows to obtain reversible accumulation of methane inside cellular nanostructures of cryogenic amorphous ice. It is important that the degree of accumulation can be sharp adjusted by pressure and temperature.

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SOME LESSONS OF THE CHEMISTRY OF METAL HYDRIDES IN THE LIGHT OF PROBLEMS OF HYDROGEN ACCUMULATION

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“Everything may be said
But not all can be realized in this World
The human fantasy is not limited by anything
But the Nature strongly limits our possibilities”
(*Olap Alpa-Pashi*)

Abstract. A number of observations and critical remarks were made dealing with perspectives of the metallic materials (both classical alloys and quasi-crystals) and nano-sized carbon materials as reversible accumulators of hydrogen.

During almost one and half century, the chemistry of metal hydrides demonstrated many interesting and instructive circumstances. We can see both experimental successes (natural and accidental) and unrealized expectations; both scientific clear-headings, successful prognoses and theories (models) which proved to be unsound; mistakes – conscientious or not; both persistent searches of truth (effectuated sometimes by the tests-and-mistakes way) and anti-science in its different manifestations – up to falsifications. Here sensations also can be seen – both true and false.

Strictly speaking, we know only two real sensations: the discovery (by Graham in 1863) of the hydrogen uptake by palladium with $\text{PdH}_{0.6}$ formation and the practically occasional discovery of the reversible absorption of hydrogen at moderate conditions by some alloys and intermetallic compounds (IMCs) (Neumann; Zijlsta & Westendorp; Wiswall & Reilly).

The false sensations appeared in the rather large quantity. In most cases they were related with the record and super-record hydrogen uptake by one or another metallic material.

The most representative between them was, undoubtedly, the very brief but bright story related with cold-fusion (CF). Many features typical for anti-science have been displayed here: the impossibility of the reproduction of the results by another independent researchers; the passing over in silence about experimental details (or refusal in their publication); non-critical attitude to own data related with the waiting of miracle (e.g., treating of the registration of mass 3 in mass-spectroscopic experiment with impure (protium-containing) deuterium as the evidence of the CF occurrence); the ignoring of natural laws (the thermodynamic impossibility of CF effectuation) and so on. Fortunately, our (Russian) scientific society has survived this story with minimal damages (regarding to scientific reputation). One can note also that our hydride science have demonstrated the wholesome immunity towards the obscurant shady transaction dealing with so-called “torsional fields” [1].

It is difficult, however, to reproach investigators (of the starting period of the IMC-hydride chemistry) with their very optimistic, excessive hopes concerning the limiting content of hydrogen (n_H) in metal hydrides. Then existing intuitive notions on factors limiting n_H (number of interstitial sites with available volume, valence possibilities of metals, "group" affinity of metals towards hydrogen, etc.) were incessantly refuted by the results of reliable experiments (synthesis under moderate conditions of VH_2 , $NdRu_2H_{5.5}$, $Ti_{1-x}W(Mo, Cr)_xH_2$; at high hydrogen pressures – of $LaCo_5H_9$, $TiCr_{1.8}H_{5.3}$, ScH_3 , NiH , CoH , RhH , MoH , etc.). These facts created sometimes the illusion that everything is possible in the field of metal hydrides. As a result, some hasty statements appeared (based on the results of the non-verified or incorrectly organized experiments) about the receiving of such hydrides as $TiH_{>2}$, $ZrH_{>2}$, $VH_{>2}$, La_4TiH_{25} . Theoretical calculations of the properties of hydrides whose existence is physically impossible (e.g., TiH_3 , $MgNiH_4$) were also performed (for details see [2, 3] and publications cited therein).

The question of super-stoichiometry (with H/M ratio exceeding 2) in hydrides of IV and V Groups is of principal significance because such hydride compositions are forbidden from the point of view of our actual knowledge [2]. Correspondingly, each such claim must be accompanied by detailed description of both synthesis and analysis procedures as well as by X-ray characterization of the "new superhydride" (including the original X-ray pattern or the table with Bragg's-reflections intensities and positions). However, these obvious requirements are always ignored in the publications under consideration. At the time, the unit-cell parameters presented in these works (see, e.g., [4]) clearly demonstrate that the corresponding hydrides are not super- but sub-stoichiometric.

At the same time, authors of such "discoveries" can propose the unrealistic Ti-D phase diagram (based on the incorrectly treated experimental results) with the violence of the phase rule [5] or present the following idea. "Regarding hydrogen vacancies as the third component of the Zr-H system, one can conditionally treat the zirconium hydrides as ternary alloys consisting of zirconium atoms, hydrogen atoms, and hydrogen vacancies" [6] (we can ask only: why this component (H-vacancies) of the chemical system does not add the extra degree of freedom reflecting in the Zr-H phase diagram). This fully absurd logic (fortunately such "brilliant" possibility remained unknown for J. W. Gibbs) make it possible to treat h.c.p.-Ti as ternary compound $TiOct_2Tet$ and b.c.c.-Ti as $TiOct_6Tet_3$ (where Oct is octahedral and Tet – tetrahedral interstices).

It is worse when the well-defined regularities of the M-H interaction (and, correspondingly, the appropriate limitations) were ignored and the experimental results, "demonstrating" the sensational data, were treated by their authors non-critically (referring to calculation methods, analysis of the hydrogen content, or simply the incompetent organization of experiment). It is fully impossible to treat the hypothetical "obtaining" of hydrides like $Ti_{0.98}Ni_{0.98}V_{0.04}H_8$ (4H/M !) in another way except the leak in synthetic device. The situation is very typical. We also have observed such cases (data on hydrogen absorption "correspond" to quaternary hydride $CeNiAlH_4$; however this is the mixture $CeH_3 + AlNi$, formed under conditions of the gentle hydrogen leak).

Not only the lack of knowledge about the M-H interaction laws leads to the efforts in vain, but also – the ignorance of early works (i.e., of corresponding literature) by scientists who have started (in hydride chemistry) after 1970. One can believe that, if the classical work by Lambert & Gates (1925) dealing with binary Pd-H system [7] would be taken into account by Flanagan & Oates, they could not explain the dependence of the value of hydrogen-pressure hysteresis (between absorption and desorption branches) via the conditions (velocity) of the approach to equilibrium by highly hypothetical "local change of R/M stoichiometry" on the surface of $LaNi_5$ -like IMCs [8].

Equally, although the effect of so-called hydrogenolysis (term was proposed by K.N. Semenenko) was known already starting from 1960 (Beck; Pebler & Gulbransen; Mikheeva et al.), later, in many works, the parameters of hydrogen sorption (thermodynamic, kinetic) of some “complex hydrides” were presented. Meanwhile, in many cases these “complex hydrides” were not individual compounds but products of hydrogenolysis – hydrogen-induced degradation of the initial metallic compounds.

Hydrogenolysis is, of course, the very regrettable process with reference to hydrogen accumulation problems. This effect makes the manipulations of the hydride properties by the variation of IMCs (within the framework of the given R-M metallic system) impossible.

However, the creative approach to the problem allows turn this “bad” process towards scientific and practical profits. Thus, basing on investigations of hydrogenolysis of IMC-hydrides and of subsequent recombination (regeneration) of starting IMCs (as a result of interaction of the hydrogenolysis products), the express and precise method of determination of thermodynamic characteristics of IMCs was developed [9]. Of those IMCs, naturally, which take part in the chain of corresponding transformations.

It must be noted, however, that the own hidden riffs exist here. Thus, basing on truly outward analogy (practically – identity) of the DTA picture in the temperature range of hydrogenolysis and recombination for the system $\text{YNi}_2\text{-H}$ from one hand and systems $\text{LaNi}_2\text{-H}$, $\text{CeNi}_2\text{-H}$, $\text{PrNi}_2\text{-H}$, and $\text{SmNi}_2\text{-H}$ from another hand, a strong mistake was made in treating the transformations occurring in the $\text{YNi}_2\text{-H}$ system. Only the reference to the “abnormal” behavior of the $\text{ErNi}_2\text{-H}$ system has allowed later to revise the results for $\text{YNi}_2\text{-H}$ system. This revision resulted in very non-trivial observations [10].

The next (more profound) step in “rehabilitation” of hydrogenolysis was made by authors of [11]. This process, together with subsequent (during heating) regeneration process, was named by the “noble” term HDDR, i.e., **hydriding - degradation** (disproportionalization) – **desorption** – **recombination**. It was shown that, in many cases, HDDR allows to obtain super-magnets with improved microstructure. We must only note here that recombination does not occur without desorption – this is the integrated, inseparable process. What is more, processes of hydrogenation and degradation also coincide at elevated temperatures.

Interesting results have been also obtained in [12], where the hydrogenolysis process in the Ti-Ni-H system was used in order to obtain the non-destructive (mechanically) hydrogen-absorbing composite material.

The possible statement that all questions (problems) of the metal-hydride chemistry are clear now to us is, of course, obviously wrong. For instance, authors cannot treat up to now some own results, such as the fully anomalous behavior of $\text{ScCo}_2\text{-hydride}$ (in view to hydrogen desorption conditions) in different gaseous media [13]; the “abnormal” (with reference to equilibrium phase diagram) phase composition of hydride and structure of one of coexisting phases in b.c.c.- $\text{TaV}_2\text{-deuterohydrides}$ [14].

At the same time, we believe that the available now lessons of the chemistry of transition metal hydrides make it possible to avoid some mistakes in another field of inorganic chemistry related with hydrogen accumulation.

One remark: talks about nano-hydrides become in fashion now. But it is necessary to realize that nearly all the metal hydrides are nano-materials initially, definitely. In the course of hydrogenation, the compact samples of metals (or IMCs) disintegrate into small particles which have (according microscopic or surface-area measurements) micro- (and not nano-) size. However, this does not speak yet for anything. These particles are not monocrystals, but – micro-sized conglomerates of nano-sized clusters (domains). These clusters have sometimes the structure, which differs from that, indicated (defined) by X-ray or neutron

diffraction [15]. After this digression we can turn to another class of compounds, perspective for hydrogen storage.

A new branch of chemistry appears under our very eyes: carbon nano-materials as hydrogen sorbents. It seems that consideration of the above-mentioned makes it possible to form a correct estimate of corresponding perspectives. We imply here both the rejection of obviously fantastic experimental results, of some theoretical conjectures and, on the contrary, such real possibilities which can be given in our disposal by this class of compounds (see [16], with references).

During the first (starting) stage of the corresponding investigations, the underestimated (in respect to hydrogen capacity) data were often caused by the lack of the appropriate preliminary treating of the sample. In addition, even samples of the given type (e.g., carbon nano-tubes) may be very heterogeneous (in view to both their characteristics and impurities). The last factor was sometimes ignored in analysis of experimental data [17].

In contrary, many factors can result in overestimation of hydrogen capacity of carbon nano-materials. Thus, the presence of water or another hydrogen-containing impurities can drastically distort the results of desorptional mass-spectroscopy or thermogravimetry, see [18, 19].

Another possible source of errors is the experimental methodology itself. It was shown that, under conditions of high hydrogen pressure and small amount of sample, the lowering (non-appreciated) of temperature by 1 K results in "increasing" of the hydrogen content by 2.6 wt. % [20]. Naturally, possible leak in experimental device also results in fatal consequences.

With all provisos to be made, the strictly verified amounts of hydrogen reversibly absorbed by carbon nano-materials (1.5-2.0 wt. %) already corresponds to those for such IMCs as LaNi_5 or TiFe (however, under essentially different conditions of the absorption-desorption process). Both theoretical approaches and some experiments demonstrate the possibility of reversible absorption of greater amount of hydrogen – up to 7 wt. % (10 wt. % in perspective). However, the growing pains (such as overestimated hopes and physically impossible waitings) are as yet inherent in this field of science [16]. It must only be discredited by such announcements as the obtaining of 67 wt.% H (cf. the "synthesis" of $\text{PdH}_{2.2}$ (!) in the same work). But this is not the reason for rejecting these compounds (as possible hydrogen accumulators) at all, as some more modest results are quite reliable and interesting.

The problem in question is really very complicated. Here we have many potential possibilities: formation of quasi-liquid hydrogen in cavities of nano-materials, physical adsorption of hydrogen molecules, absorption of H-atoms, formation-rupture of "covalent" C-H bonds with possible eluation of carbon in the form of gaseous hydrocarbons. But the complicity of the problem cannot create obstacles to the true science. As every new field, chemistry of hydrogen in carbon nano-materials requires serious and all-round experimental investigations. Only such investigations can precede to theoretical treating of the phenomenon and be the criterion of the accuracy of different theoretical constructions.

In conclusion, let us consider objects, which are, at first glance, alien to the problem under consideration.

In 1984 a very unusual metallic alloy was discovered [21]. The structure of this alloy was characterized by the simultaneous presence of the five-order symmetry and the long-range ordering of atoms (this combination is fully impossible from the point of view of classical crystallography). The active discussion, scepticism, and refusal from the side of representatives of traditional crystallography were initiated by this discovery. The accusations of both violation of the first principles and false-scientificy in treating of the obtained results were

expressed. At the same time, attempts to find the alternative explanations for corresponding experimental data (which agree with generally accepted notions) were performed. One of them belongs to Nobelian in Chemistry L. Pauling [22]. Using the X-ray powder diffraction data for $\text{Al}_{73}\text{Mn}_{21}\text{Si}_6$ alloy, he has proposed the very subtle structural model based on cubic unit cell with enormous lattice parameter (26.74 Å) containing nearly 2000 atoms! According to this model, the icosahedral symmetry (which was found for corresponding alloy by means of electron diffraction) appears as a result of many-times twinning of the cubic crystals.

After this, however, both high-resolution microphotographies and new data on electron diffraction were obtained. These data were in disagreement with Pauling's conclusion [23]. Alas, great scientists may also be wrong and only His Majesty Experiment remains the authority in science. Naturally, this experiment must be adequately organized and corresponding results must be independently reproduced.

The Shechtman's discovery has induced the proper boom in researches dealing with synthetic technologies and investigations of the structure, physical and chemical properties of these remarkable objects, which were named quasicrystals [24].

At present, a number of quasi-crystalline alloys with icosahedral, decagonal, and octagonal symmetry are synthesized by different methods. The quasi-crystalline form of the solids turned out to be widespread in a great extent. The absence of the translation symmetry and the presence of numerous interstitial sites of the different types in the structure of icosahedral quasicrystals makes some of them interesting objects for hydride chemistry. We cannot wait for any sensational discoveries here, as the general laws of M-H interaction do not depend on matrix structure. However, encouraging results were obtained for icosahedral $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ [25]. This alloy may be perspective for high-temperature accumulation of hydrogen. The corresponding investigations are in progress [26].

Thus, the numerous and instructive lessons of the well-developed field of science – chemistry of transition metal hydrides – allow to treat the results obtained for “non-traditional” materials more soberly. At the same time, these lessons call us to new enterprises.

Acknowledgements

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ABOUT INTERACTION OF HYDROGEN WITH SPHERICAL PARTICLES OF BT5-1 TYPE ALLOY

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Abstract. The interaction of hydrogen with spherical particles of an alloy such as BT5-1 containing 92.05 mass% of Ti, 4.52 mass% of Al and 3.43 mass% of Sn with diameters of particles of 0.1, 0.4, 0.6 and 0.8 mm was investigated at temperatures of 773–973 K and pressure of 1–6 MPa. It was shown that the alloy has the lower absorbed capacity on hydrogen in comparison with titanium and thermal stability of the hydrogenated alloys is lower than a stability of titanium dihydride.

Keywords: Titanium alloy with aluminum and tin; Spherical particles; Thermal stability; Absorbed capacity on hydrogen

1. Introduction

Titanium and its alloys find a wide application in a science and engineering. At the increased temperatures they react actively with gas impurities present in an atmosphere, forming thus a number of solid solutions and the phases of introduction, which essentially change the original physico-chemical and physico-mechanical properties of initial alloys. So, in a case with hydrogen the embrittlement of titanium-containing alloys occurs. In the literature there is a number of theoretical and experimental works describing an influence of hydrogen on processes of hydrogenation and brittle failure of various metals and alloys, for example [1–4].

In the present work the experimental data about interaction of hydrogen under pressure of 1–6 MPa at the temperatures 773–973 K with spherical particles of an alloy on a basis of titanium such as BT5-1 are submitted.

2. Experimental

The researched alloy as spherical particles by a diameter of 0.1, 0.4, 0.6 and 0.8 mm contained, on the data chemical and microröntgenospectral analyses, 92.05 mass% of Ti, 4.52 mass% of Al and 3.43 mass% of Sn. According to the results of the X-ray phase analysis, the initial alloy is homogeneous and represents a solid solution of aluminum and tin in α -titanium which crystallizes in a

hexagonal syngony with the following parameters of a lattice: $a = 0.2959 \pm 0.0002$ nm, $c = 0.4670 \pm 0.0003$ nm.

The hydrogenation of an alloy was carried out in laboratory plant of high pressure on the following technique. An alloy as spherical particles of weight of ~ 5 g was washed out by ethanol and ether, was loaded into a reactor-autoclave and was evacuated for 0.5 h at 773 K up to residual pressure of ~ 1 Pa. Then at same temperature into reactor hydrogen of high cleanliness from the hydrogen accumulator containing as a working material hydride phase on a basis of intermetallic compound LaNi_5 was brought up to a pressure of 1–6 MPa. The ending of reaction was determined on the termination of pressure fall in the calibrated system. After cooling of reactor in an atmosphere of hydrogen up to room temperature the composition of received hydride phases was established. If necessary realizations of several cycles of sorption-desorption of hydrogen a removal of hydrogen from received hydride phases was carried out under a vacuum of ~ 1 Pa at temperatures of 823–873 K for 1 h. The reaction products were unloaded in an inert atmosphere and were analyzed.

Pressure of hydrogen was measured by standard manometer of a class accuracy of 0.4.

The composition of hydride phases was established by methods of gas volumetric and chemical analyses. The mistake of definition did not exceed 1 %.

X-ray graphical investigations were performed on an automatic assembly including a diffractometer DRON-UM-1 ($\text{Cu K}\alpha$ -emission) and the managing computer. The error of definition of interplanar spacing did not exceed 0.0005 nm.

Morphology of particles of an initial alloy and hydrogenation products was investigated on electronic focused beam microscope MREM-100.

Thermographic investigations were carried out on synchronous thermoanalyzer STA-409 PC in a polythermal regime in an interval of temperatures of 293–1273 K with speed of heating of 10 degrees/min in a argon current of the high cleanliness.

Microhardness of samples was determined on microdurometer PMT-3 at loading of 50 g.

All work with hydrogenation products was spent in an argon atmosphere of the high cleanliness.

3. Results and Discussion

The interaction results of samples of an alloy BT5-1 with hydrogen are given in Table 1.

The hydrogenation of spherical particles of an alloy BT5-1 proceeds without the induction period at 773 K with exothermic effect, therefore a temperature in autoclave raises up to 820 K (sample 1–4). The content of hydrogen in hydrogenation products answers the composition $\text{Ti}(\text{Al}, \text{Sn})\text{H}_{1.8}$. On the diffractograms of products of hydrogenation only the reflexes of titanium hydride are observed with the constant of a crystal lattice $a = 0.4434\text{--}0.4437$ nm (for $\text{TiH}_{1.92}$ $a = 0.4448$ nm). The reduction of a diameter of alloy particles results in appreciable decrease of time of sample saturation by hydrogen: with 4 h at a diameter of particles of 0.8 mm (sample 4) up to 10 min at a diameter of particles of 0.1 mm (sample 1). At that the density of titanium doped by Al and Sn in

process of saturation of its by hydrogen decreases and becomes equal $3.82 \pm 0.03 \text{ g/cm}^3$ for the composition $\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$.

TABLE 1. Conditions and investigation results of hydrogenation of spherical particles of an alloy BT5-1

Sample no.	Sphere diameter, mm	Conditions of interaction			Chemical composition of interaction products	Phase composition of interaction products	Lattice constants of titanium hydride a (nm)
		P (MPa)	T (K)	Time (h)			
1	0.1	1	820	0.17	$\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$	$\text{TiH}_{1.8}$	0.4437
2	0.4	1	820	2.0	$\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$	$\text{TiH}_{1.8}$	0.4436
3	0.6	1	820	2.5	$\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$	$\text{TiH}_{1.8}$	0.4437
4	0.8	1	820	4.0	$\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$	$\text{TiH}_{1.8}$	0.4434
5	0.8	6	973	4.0	$\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$	$\text{TiH}_{1.8}$	0.4436
6	0.1	6	973	4.0	$\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$	$\text{TiH}_{1.8}$	0.4437

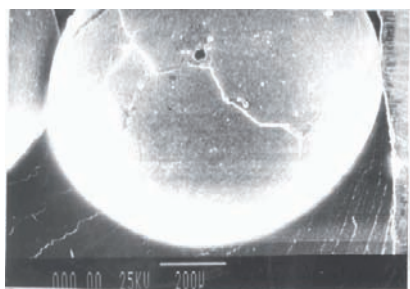
In Fig. 1 the microphotos of spherical particles of an alloy BT5-1 by a diameter of 0.6 mm are submitted in an initial condition (a) and after realization of one (b), five (c) and ten (d) cycles of sorption-desorption of hydrogen.

It was established that already after the first cycle of sorption-desorption of hydrogen about 90% of particles of an initial alloy become covered by cracks, after 5 cycles – 100%. With increasing amount of cycles (from 1-st to 10-th) there is also simultaneous deepening cracks and breaks. As a rule, process of hydrogenation and accompanying phenomenon of a formation of cracks are connected to defects (bowls and breaks) of the surfaces of initial samples. The similar picture is observed and for spherical particles of an alloy with other sizes.

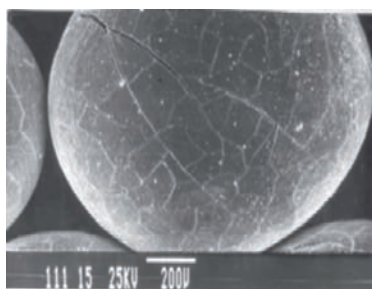
The hydrogenation of particles of an alloy BT5-1 in hard conditions – at temperature of 973 K and pressure of hydrogen up to 6 MPa (samples 5–6) – does not result in increase of the content of hydrogen in an alloy: it remains former and corresponds to composition $\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$.

The thermal stability of hydrogenation products $\text{Ti}(\text{Al},\text{Sn})\text{H}_{1.8}$ is lower, than a stability of titanium dihydride. On samples thermogravigrams three endothermal effects are observed, and besides ~20% of the hydrogen absorbed by an alloy is isolated already at 783 K and 823 K, and the most part of the stayed hydrogen is isolated at 900 K.

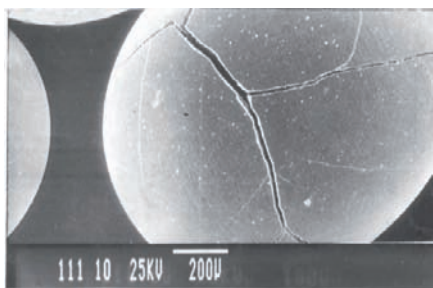
For initial alloy and the hydrogenation products the values of microhardness are measured, which have appeared equal 337 ± 50 and $565 \pm 51 \text{ kg/mm}^2$, accordingly. The microhardness of the samples which have stayed after realization



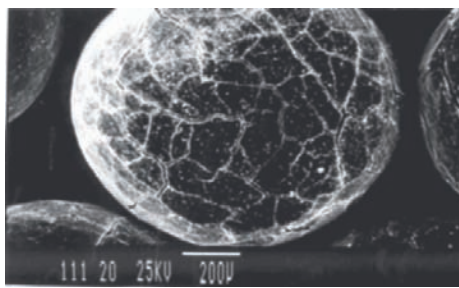
a



c



b



d

Figure 1. Microphotos of spherical particles of an alloy BT5-1 by a diameter of 0.6 mm in an initial condition (a) and after realization one (b), five (c) and ten (d) of cycles of sorption-desorption of hydrogen (increase $\times 75$).

of the differential thermal analysis (DTA) makes $467 \pm 44 \text{ kg/mm}^2$, that does not contradict the results of the chemical analysis on hydrogen content. The samples of alloy BT5-1 after realization of DTA have the composition $\text{Ti(Al,Sn)H}_{0.01-0.02}$.

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APPLICATION OF LAYERED InSe AND GaSe CRYSTALS AND POWDERS FOR SOLID STATE HYDROGEN STORAGE

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Abstract. Processes of hydrogen electrochemical intercalation into layered InSe and GaSe crystals and its deintercalation were investigated. It was ascertained that for concentrations $x < 2$ hydrogen mainly enters in interlayer space and forms H_2 molecules, where x is the amount of introduced atoms per one formula unit of the crystal bulk. For $2 < x < 4$ atomic hydrogen being built into interstices due to quantum-size effects for the gap and H_2 molecules. Deintercalation of hydrogen from $H_x\text{InSe}$ and $H_x\text{GaSe}$ crystals was carried out for 3÷9 hours at $T = 110^\circ\text{C}$ using permanent pumping out. Degree of their deintercalation increases linearly from 60% at $x \rightarrow 0$ up to 80÷85% at $x \rightarrow 4$. Investigation of InSe and GaSe crystal powders has shown that x can easily reaches $x = 5 \div 6$ and deintercalation achieved values up to 90%. Conducted at $T = 80\text{K}$ optical investigation of exciton absorption spectra shown that repeated cycles of hydrogen intercalation-deintercalation do not result in essential worsening of physical parameters of InSe and GaSe crystals.

Keywords: hydrogen, hydrogen storage, layered crystals, InSe, GaSe, intercalation, exciton, QW.

1. Introduction

Layered InSe and GaSe crystals attract investigator interest because of heterostructures based on them possess good photosensitivity and find their application in solar cells [1-3]. At the same time distinctive feature of layered crystals - sharp anisotropy of chemical bonds (strong ion-covalent inside crystal layers and weak van der Waals between them) paid great attention of researchers to intercalation, that is to insertion of atoms and molecules into interlayer space of a layered crystal - the so-called «van-der-Waals gap». In particular for InSe and GaSe crystals volume of van der Waals gap makes under the attitude to all volume of a crystal about 40÷45 %.

Therefore layered InSe and GaSe crystals are rather promising for hydrogen energetic as operating elements in systems for hydrogen accumulation [4, 5]. The concentration of hydrogen in them can reach values $x = 3 \div 4$, where x is the amount of introduced atoms per one formula unit of the crystal bulk.

This work consist of a two adding one another experimental parts, discussion and conclusions. In the first experimental part, we report about our investigations of hydrogen intercalation-deintercalation processes in layered InSe and GaSe crystals and powders. In the second one, the influence of intercalated hydrogen on optical properties of these crystals is reported.

2. Experimental

Layered InSe and GaSe crystals belong to A^3B^6 binary compounds. The layers in them consist of four Se-In(Ga)-In(Ga)-Se sheets with three Se atoms coordinated to one In(Ga) atom that corresponds to spatial group D_{3h}^1 (see Fig. 1). The covalent In(Ga) - In(Ga) bonds are oriented perpendicular to the layers. Bridgman grown InSe and GaSe crystals have four (β -, δ -, ε - and γ -) polytypes [6, 7], which differ by sequence of layers stacking. Thus bulk InSe single crystals are of the γ -polytype with a rhombohedral (trigonal) crystal structure (space group C_{3v}^5 , one In_2Se_2 molecule in the primitive unit cell). The conventional hexagonal unit cell extends over three layers and consists of three In_2Se_2 molecules. GaSe single crystal had ε -polytype. It belong hexagonal crystal structure (space group D_{3h}^1) which primitive unit cell consists of two Ga_2Se_2 molecules (eight atoms) located within two crystal layers [7].

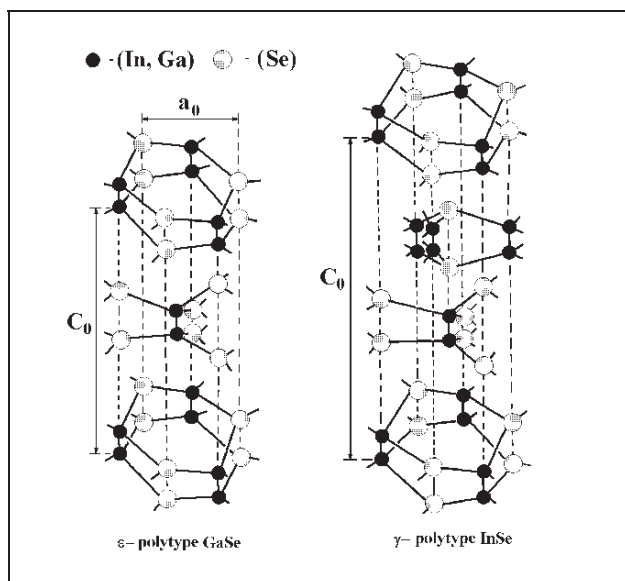


Figure 1. The crystal structure and stacking of a crystal layers in γ -InSe and ε -GaSe.

Lattice parameters of γ -InSe and ε -GaSe crystals are well known. For ε -GaSe they are: $C_0 = 15.95\text{\AA}$ and $a_0 = 3.755\text{\AA}$ [8]. For γ -InSe they are: $C_0 = 25.32\text{\AA}$ and $a_0 = 4.001\text{\AA}$. Interlayer nearest-neighbour distances in layers (see Fig. 2a) are

$C_{\text{In-In}} = 2.79 \text{ \AA}$ and $C_{\text{In-Se}} = 2.65 \text{ \AA}$, respectively; $\angle \varphi = 119.3^\circ$, the layer thickness $C_1 = 5.36 \text{ \AA}$, the distance between layers $C_i = 3.08 \text{ \AA}$ and their interlayer distance $C_{\text{Se-Se}} = 3.80 \text{ \AA}$ [9, 10].

2.1. INTERCALATION

Samples investigated in present work were obtained by cleavage of crystal plates from bulk γ -InSe and ϵ -GaSe single crystals with the help of usual blade. Owing to weak van-der-Waals chemical bond one could easily obtain crystal plates of a necessary thickness with parallel mirror surfaces not requiring polishing and etching. To combine hydrogen intercalation with optical investigations, samples of $10 \div 20 \mu\text{m}$ thickness was prepared. The powders with size of grains about $5 \div 20 \mu\text{m}$ were obtained from the ingot of γ -InSe and ϵ -GaSe crystals in ultrasonic mill. Then for the next intercalation the crystal powders were compressed into tablets.

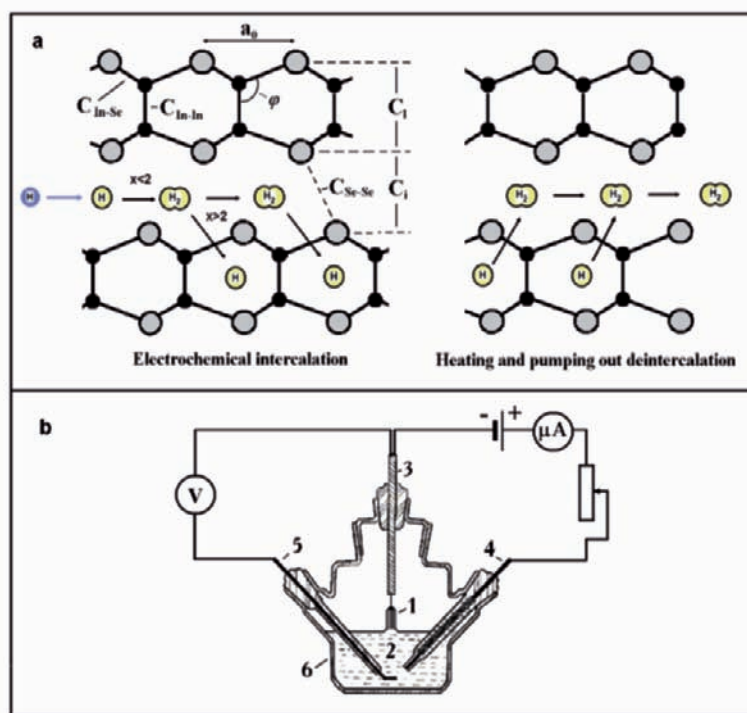


Figure 2. a - 2D sketch illustrate processes of intercalation and deintercalation of hydrogen in layered crystals like InSe and GaSe.

b - schema of electrochemical cell: 1- layered crystal; 2 - electrolyte; 3- working platinum electrode; 4- electrode of comparison (AgCl); 5 - auxiliary platinum electrode; 6 - cell body.

In process of intercalation a three-electrode glass cell from a chemically and thermic stable glass consisting (see Fig. 2b) from an electrode of comparison (AgCl), working and auxiliary (platinum wire) electrodes were used. Investigated

sample was soldered with a working electrode by a wire and immersed in electrolyte – the 0.1 normal solutions of hydrochloric acid obtained from bidistilled water and chemically pure concentrated hydrochloric acid.

Hydrogen intercalation of γ -InSe and ε -GaSe samples was carried out (like as in [4, 5]) using the electrochemical method from electrolyte with sweeping electric field in the galvanostatic regime. A special “soft” choice of the optimal electric field strength and current density ($E = 30 \div 50$ V/cm and $j \leq 10$ $\mu\text{A}/\text{cm}^2$) enabled to obtain homogeneous in their composition intercalated with hydrogen H_xInSe and H_xGaSe crystal samples for concentrations $0 < x \leq 4$ and powders of a given crystals for $0 < x \leq 6$. The hydrogen concentration was determined via the quantity of electrical charge transported through the sample placed into the cell.

Also it was established, that the preliminary irradiation by the laser beam with $\lambda = 1.06\mu\text{m}$, in particular of GaSe crystal samples, in 1.5 time increase the speed of hydrogen intercalation in these crystals.

We assume that at low concentrations atomic hydrogen enter into the van der Waals gap by the presented on the Fig. 2a schema and creates H_2 molecules that occupy an ordered positions schematically shown in Fig. 2a. Appearance of hydrogen molecules in the gap, result in occurrence of interlayer pressure and in increasing of interlayer parameter C_0 . At higher concentrations atomic hydrogen incorporate into the crystal layers.

Starting from this concept, let us estimate the concentration and pressure of H_2 molecules in the van-der-Waals gap of H_xInSe at $x = 2$. As the volume of γ -InSe conventional hexagonal cell is equal $V = 351 \text{ \AA}^3$, the concentration of elementary cells is $N_0 = 1/V = 2.85 \cdot 10^{21} \text{ cm}^{-3}$. At $x = 2$, one H_2 molecule corresponds to one In_2Se_2 molecule. Hence, H_2 molecular concentration is equal $N = 3N_0 = 8.55 \times 10^{21} \text{ cm}^{-3}$. Using Clapeyron's equation for the ideal gas pressure $P = Nk_B T$, where k_B is the Boltzmann constant and T is the absolute temperature, we can deduce that the pressure caused by H_2 molecules in InSe van-der-Waals gap is equal to 9.4 MPa at $T = 80\text{K}$ and 35.4 MPa at $T = 300\text{K}$.

The dependence of γ -InSe crystal parameters on pressure is studied rather well. In accord with [10], the hydrostatic pressure increase of 10^5 to 8×10^9 Pa results in essential drop of the van-der-Waals gap due to the decrease of the distance $C_{\text{Se-Se}}$ from 3.8 $\text{\AA}$ down to 3.3 $\text{\AA}$ (13%). In this case, the distance $C_{\text{In-In}}$ decreases from 2.79 $\text{\AA}$ down to 2.69 $\text{\AA}$ (3.58%), $C_{\text{In-Se}}$ from 2.65 $\text{\AA}$ down to 2.59 $\text{\AA}$ (2.26%). However, as a consequence of the angle $\angle\varphi$ growth from 119.3° up to 121.3° (1.5%), the width of the crystal layer C_1 decreases only by 0.26% from 5.36 $\text{\AA}$ down to 5.345 $\text{\AA}$.

Performing an extrapolation of results [10] in our case, when H_2 molecules do not compress but flare layer packages, we can estimate that under the pressure $P = 35.4$ MPa ($x = 2$, $T = 300\text{K}$) the distance $C_{\text{Se-Se}}$ should increase from 3.8 $\text{\AA}$ up to 3.808 $\text{\AA}$, and the constant C_0 of γ -InSe crystal should grow, respectively, by 0.024 ± 0.001 $\text{\AA}$; at $P = 9.4$ MPa ($x = 2$, $T = 80\text{K}$) C_0 grows by 0.009 ± 0.001 $\text{\AA}$.

Really, conducted in present work X-ray diffraction study of H_xGaSe crystals at $T = 300\text{K}$ shown that parameter C_0 growth with x and at $x = 1.0$ increased by 0.031 ± 0.003 $\text{\AA}$ from $C_0 = 15.94 \text{\AA}$ to $C_0 = 15.971 \text{\AA}$. It is in 2.5 times greater than one can estimate from our simple pressure extrapolation. At the same time one can observe an insignificant growth of a crystal lattice parameter a_0 with x . Thus for

$x = 1.0$ a_0 increased by 0.006 ± 0.003 Å from $a_0 = 3.753$ Å up to $a_0 = 3.759$ Å. This results evidenced that: i) even for $x < 2$ hydrogen are able to penetrate into a layer space; ii) magnification of C_0 due to pressure created by impurities in the van der Waals gap happens much faster than diminution of C_0 and a_0 due to similar hydrostatic pressure. Note that such a pressure of atoms or molecules at significant degree of their intercalation in layered crystal can lead to exfoliation of layered crystal [11].

Before the following discussion of absorption spectra, let us note several important points that are worth to be considered.

1. For H_2 molecule, the critical temperature T_r at which freezing-out of rotational modes begins is equal to 90K, in accordance with the classical expression $T_r = \hbar^2/8\pi^2 \cdot J \cdot k_B$, where $J = mr^2$ is the rotational moment of inertia for this molecule, $m = 3.34 \cdot 10^{-27}$ kg is H_2 molecule mass, $r = 0.74 \cdot 10^{-8}$ cm means H_2 molecule radius, $\hbar$ and k_B are Planck's and Boltzmann's constants, respectively. When $T < T_r$, the quantity of rotating H_2 molecules begins to reduce rapidly, however, even at lower temperatures it remains above zero as a consequence of the Maxwell velocity distribution for molecules.

2. As seen from Fig. 2a, the van der Waals gap width is modulated periodically: in positions of In atoms it is larger than in positions of Se atoms. This gap can be described as a layer of closely packed parallelepipeds, at the both ends of which pyramids are placed. The volume of this body (cavity) is equal to 50.5 Å^3 , and for an ideal crystal, when defects of the dislocation type are absent the relative gap volume comprises 43% of the crystal bulk. It is obviously larger than the lower estimate 37% obtained using the ratio $C_i/(C_i+C_l)$.

3. Geometrical sizes of H_2 molecule and van der Waals gap width of InSe crystal have such values that cause quantum-size effects. Using the well-known expression [12] for localization of a particle in the quantum well with infinite rectangular walls

$$E = \frac{\pi^2 \hbar^2}{2d^2 M} , \quad (1)$$

and taking d as the gap width $C_i = 3.08$ Å as well as M being the H_2 molecule mass, we can deduce the value of the localization energy $E = 1.1$ meV. This dimensional quantizing implies that in one state (cavity), according to the Pauli principle, more than two (Fermi particles) H_2 molecules with opposite directions of their spins (similar to para- and orthohydrogen) cannot be placed. However, H_2 molecule and cavity sizes have such values that more than one molecule cannot be arise in this cavity. In the opposite case, H_2 molecule outer shells should be taken up with each other till distances approximately $1.5 \div 2$ Å and fixed in this position. But it is hardly possible in view of their strong repulsion. Therefore at $x > 2$, the only one H_2 molecule remains, while abundant atomic hydrogen should penetrate into interstices of crystal layers, which is confirmed by NMR investigations [13, 14] with the clear evidence of hydrogen entering into interstices of GaSe at $x > 2$.

4. In accord with [15], under conditions: $P = 9.4$ MPa and $T = 80K$, the quantity of hydrogen being in a condensed state is approximately 18%, while

considering effect of cooling H_2 molecules due to their localization in the gap plane, one can expect that the quantity of liquid hydrogen in gap can reach up to 25%.

5. The important factor that improve process of hydrogen intercalation in layered crystals is that the molecular hydrogen at temperatures lower than 4K is in a solid state phase having a dense hexagonal lattice of a D_{6h}^4 spatial group with parameters: $a_{H_2} = 3.75 \text{ \AA}$ and $C_{H_2} = 6.12 \text{ \AA}$ [16]. Note, that the same spatial group has β -GaS crystal [6, 7].

It is seen that the arrangement of H_2 molecules in van der Waals gap of GaSe ($a_0 = 3.755 \text{ \AA}$) and InSe ($a_0 = 4.001 \text{ \AA}$) crystals coincides with parameter a_{H_2} . Moreover the packing of H_2 molecules between adjacent crystal layers also corresponds to D_{6h}^4 spatial group. However parameters $C_{GaSe} = C_0/2 = 7.98 \text{ \AA}$ and $C_{InSe} = C_0/3 = 8.44 \text{ \AA}$ for H_2 molecules in the gap of GaSe and InSe crystals are accordingly in 2.6 and 2.8 time greater than parameter C_{H_2} .

With dielectric permeability for the region of crystal lattice vibrations of InSe ($\epsilon^\perp = 6.8$) and GaSe crystals ($\epsilon^\perp = 6.2$) [17] it is not difficult to show that appearance of a crystal layer between two H_2 molecular sheets lead to screening of their interaction. It results in increase of parameter C_{H_2} in a matrix of a layered crystal, which becomes practically continuous with parameter C_{GaSe} and C_{InSe} in the given crystals.

This preliminary discussion enabled us to draw the following conclusions:

When x increased up to 2, H_2 molecules have a tendency to fill in the van-der-Waals gap of layered InSe and GaSe crystals all translation ordered positions. It causes a pressure resulting in growing C_0 parameter of layered crystal. At $T = 80K$, when rotation of H_2 molecules is practically absent, and there is a clear tendency to ordering, this state of molecular hydrogen in van der Waals gap can be titled as the state of a «quasi-liquid monolayer». At temperatures of liquid helium molecular hydrogen in the van der Waals gap and layer crystal forms a superlattice consisting from a layered crystal lattice and a lattice of molecular hydrogen cryocrystal built in its van der Waals gap. For H_xGaSe crystal the periods of GaSe crystal and H_2 cryocrystal practically coincide.

At $x > 2$ atomic hydrogen begins to incorporate into interstices of the crystal lattice due to quantum-size effects in the gap and that of H_2 molecules repulsion.

2.2. ABSORPTION

Investigations of H_xInSe and H_xGaSe crystals absorption spectra were carried out at $T = 80K$ using the $\frac{1}{2}m$ spectrometer with 600 grid/mm diffraction grating and resolution not worse than 0.5 meV. As a light source, we used incandescent filament lamp supplied from the stabilized direct current unit.

InSe and GaSe crystals are characterized with a weak interaction of 3D Wannier excitons with homopolar optical A' -phonons [18, 19]. Therefore, when calculating the exciton absorption spectra, we took into consideration effects of broadening the exciton states using the standard convolution procedure (see in [18]) for theoretical values of $\alpha(\hbar\omega)$ the absorption coefficient in the Elliott's model [20] with $f(\hbar\omega) = \Gamma / [\pi(E^2 + \Gamma^2)]$ the Lorentzian function in the Toyozawa's model [21], where Γ is the half-width at half-maximum which is usually associated with the lifetime $\hbar/2\Gamma$.

The half-width at a half-maximum of a ground ($n = 1$) and excited ($n > 1$) exciton absorption bands at fixed temperatures in general form were obtained in [22]

$$\Gamma_i^2(T) = \Gamma_i'^2(T) + \Gamma_{inh}^2 = \Gamma_i'^2(0) \cdot [\Theta_i + \beta_i' \cdot n^*(T)]^2 + \Gamma_{inh}^2, \quad (2)$$

where index $i = 1, 2, 3 \dots n \dots c$ attributed with ground ($n = 1$), excited ($n > 1$) and continual ($c = \infty$) exciton states, and parameters

$$\beta_i' = \begin{cases} \sqrt{2}[(\beta_i^2 - 1)/\beta_i] & \text{at } n > 1 \\ \beta_i & \text{at } n = 1 \end{cases}, \quad \Theta_{n=1} = \begin{cases} \sqrt{2} & \text{at } R_0 > \hbar\Omega \\ 1 & \text{at } R_0 < \hbar\Omega \end{cases}, \quad \Theta_{n>1} \equiv 1.$$

In Eq. (2) Γ_{inh} is the temperature independent additive inhomogeneous component of the exciton absorption band half-width. It does not depend on temperature and is due to exciton scattering on the crystal lattice defects; $\Gamma_i'(T)$ is the homogeneous component. It increases with crystal temperature and is due to exciton scattering by phonons. $\Gamma_i'(0) = g^2[\hbar\Omega(R_0/i^2 - \hbar\Omega)]^{1/2}$, where g is the exciton-phonon coupling constant. $n^*(T) = [\exp(\hbar\Omega/k_B T) - 1]^{-1}$; k_B is the Boltzmann constant; $\beta_i = 1 + [(R_0/i^2 + \hbar\Omega)/(R_0/i^2 - \hbar\Omega)]^{1/2}$; R_0 is the exciton binding energy; $\hbar\Omega$ is the energy of effective phonon at which exciton is being scattered. As well as for InSe and GaSe $R_0 > \hbar\Omega$ then in Eq. (2) $\Theta_{n=1} = \sqrt{2}$.

For evaluation of correct values for homogeneous half-width of ground $\Gamma_1'(0)$, excited $\Gamma_n'(0)$ and continual $\Gamma_c'(0)$ exciton states at $T = 0$ the dependence

$$\Gamma_n'(0) = \Gamma_c'(0) - [\Gamma_c'(0) - \Gamma_1'(0)]/n^2 \quad (3)$$

obtained in [22] where taken into account. Note that Eq. (3) obtained from a semiclassical principles is a common case for experimental dependence $\Gamma_n' = \Gamma_c' - (\Gamma_c' - \Gamma_1')/n^2$ obtained by Le Toulec et al in [23]. In more detail fitting procedure of our calculation spectra to experimental exciton absorption of InSe and GaSe crystals has been described in [18, 19].

As the influence of hydrogen intercalation on optical properties of $H_x\text{InSe}$ crystals is more expressed we shall present for them exciton absorption spectra and then generalize them on $H_x\text{GaSe}$ crystals. Open circles in Fig. 3a show the absorption spectrum of $H_{0.07}\text{InSe}$ crystal at $T = 80\text{K}$, partial reflection of the incident onto the crystal light being taken into consideration ($n_0 = [n_0^{\perp 2} \cdot n_0^{\parallel}]^{1/3} = 3.5$ [18]). There also represented are the following absorption bands: $n = 1$ (curve 1) and $n = 2$ (curve 2) for exciton states, band-to-band transition (curve 3) and the shallow defect level situated by 45 meV lower than the conduction band (curve 4). The curve 5 was drawn taking into consideration the contribution of exciton states for $n = 1$ to $n = 4$, band-to-band transition, shallow defect level (45 meV) and deep trap level situated by 130 meV above the valence band top. It describes reasonably the experimental absorption spectrum of $H_{0.07}\text{InSe}$ crystal.

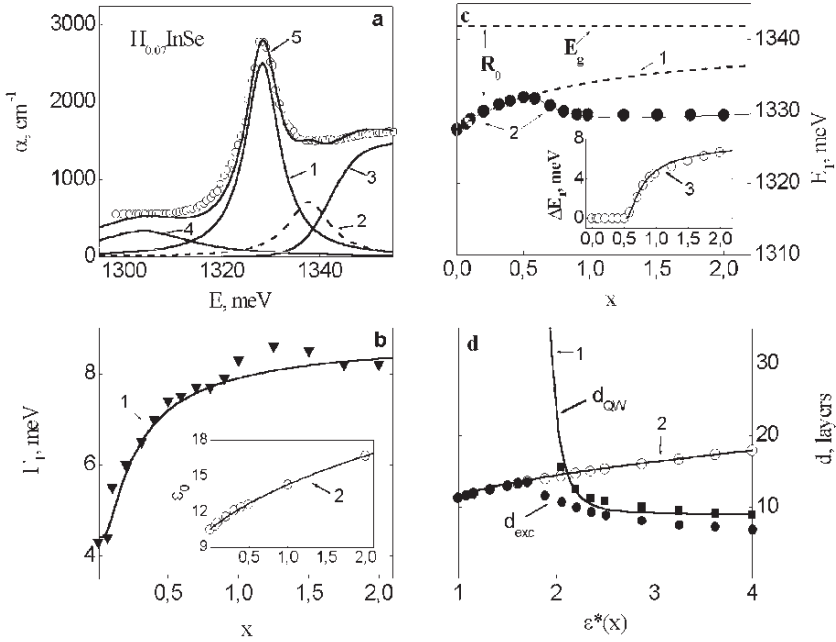


Figure 3. Exciton absorption spectra of $H_x\text{InSe}$ at $T = 80\text{K}$.

a – open circles experimental and curve 5 calculated exciton absorption spectra of $H_{0.07}\text{InSe}$ crystal at $T = 80\text{K}$. Curves 1 - 4 are the bands of $n = 1, 2$ exciton states, of band-to-band transition and of a shallow donor states.

b – solid triangles experimental Γ_1 dependence on x . Curve 1 - plotted in accordance with Eq.(6). On insert – open circles experimental ε_0 dependence on x . Curve 2 - plotted according to Eq. (10).

c – solid circles experimental shift of $n = 1$ exciton absorption band maximum E_1 on x . Curve E_g show the stable energy position of E_g on x increase. Curve 1 - plotted in accordance with Eq. (5), curve 2 with account of exciton localization in layer plane. R_0 – show decrease of exciton binding energy with x , when exciton localization ignored. On insert - open circles experimental dependencies of ΔE_1 on x . Curve 3 plotted in accordance with Eq. (14).

d – solid squares experimental values for quantum well thickness d_{QW} on $\varepsilon^*(x)$ parameter. Circles and solid circles - experimental dependencies for exciton diameter d_{exc} on $\varepsilon^*(x)$ parameter without and with the account of exciton localization. Curve 1 and 2 plotted according to Eq.(1) and Eq. (11).

The experimental value $K_1 = 40 \text{ eVcm}^{-1}$ corresponding to the integral intensity of $n = 1$ exciton absorption band in $H_{0.07}\text{InSe}$ crystals at $T = 80\text{K}$ and $\Gamma_1 = 4.4 \text{ meV}$ is practically equal to K^0 - the classical value for InSe crystal ($K_1 = 44 \text{ eVcm}^{-1}$), which is in full accordance with the analytical dependence of K_1 on half-width Γ_1 obtained in [18] for InSe crystals:

$$K_I(\Gamma_1) = K^0 \cdot \sqrt{\Gamma_1^2 - 2\Gamma_1^{/2}(0)} / \Gamma_1. \quad (4)$$

Therefore, we shall assume that polariton effects associated with K_1 growth do not take place, and $K_1 \cong K^0$.

At the same time, when introducing hydrogen into interlayer space of InSe crystals, one can observe the following peculiarities:

Even at $x = 0.07$ (see Fig. 3c), the exciton absorption band $n = 1$ is shifted to short-wave side by 0.8 meV relatively to that of pure InSe crystal. Note that the energy position E_1 of the exciton absorption peak with $n = 1$ for pure InSe crystal at $T = 80K$ is in full accordance with the analytical dependence:

$$E_1(T) [\text{meV}] = 1336.7 - 65/[\exp(162/T)-1] \quad (5)$$

obtained in [24] for the shift of the forbidden gap with temperature in the range $T = 4.2 \div 300K$.

Further increase of the hydrogen concentration results in a non-monotonic shift of the band in the whole and its peak in particular. In Fig. 3c, depicted with open circles is the experimental dependence of E_1 on x for $H_x\text{InSe}$ crystals. For instance, in the range $0 < x \leq 0.5$, the peak energy position shifts upward by $\Delta E_1 = 4.5$ meV from $E_1 = 1327.5$ meV up to $E_1 = 1332.0$ meV; at $0.5 < x \leq 1$ one can observe its decrease down to the energy $E_1 = 1329.5$ meV; the further increase of hydrogen amount in interlayer space does not result in changing $E_1(x)$ values.

Along with E_1 shift, we observed the change of the half-width Γ_1 of the exciton absorption band $n = 1$ with the growing hydrogen concentration. In Fig. 3b solid triangles is $\Gamma_1(x)$ dependence. It can be seen that Γ_1 increases with x in the range $0 < x \leq 1$ and at $x > 1$ becomes practically constant. The experimental $\Gamma_1(x)$ dependence can be represented with the following function:

$$\Gamma_1(x) [\text{meV}] = \Gamma_1 \cdot \{1 + 1/\exp[1/(\Gamma_1 \cdot x)]\}, \quad (6)$$

where $\Gamma_1 = 4.4$ meV.

The marked peculiarities of nonlinear shift of $n = 1$ exciton absorption band maximum at $T = 80K$ with hydrogen concentration are observed as well in $H_x\text{GaSe}$ crystals. However in $H_x\text{GaSe}$ these phenomena are less pronounced. Thus in the range $0 < x \leq 0.8$, the peak energy position shifts upward by $\Delta E_1 = 3.0$ meV from $E_1 = 2099.0$ meV up to $E_1 = 2102.0$ meV; at $0.8 < x \leq 1.5$ one can observe its decrease down to the energy $E_1 = 2100.5$ meV; the further increase of hydrogen amount in interlayer space does not result in changing $E_1(x)$ values. Simultaneously with $E_1(x)$ nonlinear shift experimental dependence Γ_1 also increases with x in the range $0 < x \leq 1.5$ and at $x > 1.5$ becomes practically constant. For $H_x\text{GaSe}$ the experimental dependence $\Gamma_1(x)$ is in accordance with Eq.(6) for $\Gamma_1 = 3.6$ meV.

2.3. DEINTERCALATION

Deintercalation of hydrogen from $H_x\text{InSe}$ and $H_x\text{GaSe}$ crystals was carried out for $3 \div 9$ hours at $T = 110^\circ C$ using permanent pumping out. Comparing $E_1(x)$ dependencies in intercalated samples with those obtained after deintercalation (see curve 2 Fig. 3c), we ascertained that the intercalation degree of $H_x\text{InSe}$ samples

grows linearly from 60% at $x \rightarrow 0$ up to 75-80% at $x \rightarrow 2$ with increasing the hydrogen concentration. The same data were obtained for GaSe crystals.

Further increasing of hydrogen concentration shown that in all range from $x = 0$ up to $x \rightarrow 4$ degree of $H_x\text{InSe}$ and $H_x\text{GaSe}$ deintercalation increases linearly from 60% at $x \rightarrow 0$ up to 80-85%. Investigation of InSe and GaSe crystal powders has shown that x can easily reaches $x = 5 \div 6$ and deintercalation achieved values up to 90%. Conducted at $T = 80\text{K}$ investigation of exciton absorption spectra of $H_x\text{InSe}$ and $H_x\text{GaSe}$ crystals shown that repeated cycles of hydrogen intercalation-deintercalation in the range $0 < x < 2$ do not result in essential worsening of physical parameters of InSe and GaSe crystals.

3. Discussion

At first we shall carry out discussion with the account of experimental data obtained for InSe crystals and then generalize them on InSe and GaSe crystals.

The observed in InSe crystals short-wave shift of E_1 with x growth could be explained in a most simple way by a change of the forbidden gap E_g with the pressure growth, this pressure being caused by hydrogen in interlayer space. Moreover, as shown in [9, 25], $E_g(P)$ dependence in $\gamma\text{-InSe}$ crystals is non-monotonic. For example, under hydrostatic pressures of 10^5 to 4.2×10^8 Pa in $\gamma\text{-InSe}$ crystals, E_g decreases by 3.3 meV, but with the following pressure increase it grows, too.

As was shown in the previous part, the hydrogen concentration increase up to $x = 2$ gives rise to the pressure between layers up to $P = 9.4$ MPa at $T = 80\text{K}$, which stimulates an increase of the van der Waals gap. Making extrapolation in accord with the analytical dependencies [9, 25], we obtained E_g growth by 0.2 meV at $P = 9.4$ MPa. At $x = 0.5$ and $T = 80\text{K}$, this increase is $\Delta E_g = 0.05$ meV. The shift $\Delta E_g = 4.5$ meV could take place under the pressure of molecular hydrogen on layer packages $P = 205$ MPa. Indeed, hydrogen can provide this pressure at $x = 12$ and $T = 300\text{K}$ but with the only condition that for $x > 2$ it does not penetrate into interstices of InSe layer packages and contains six H_2 molecules in the cavity. Hence, we made the conclusion that the observed short-wave shift of E_1 by 4.5 meV cannot be caused by a baric shift of E_g .

It is also known [26] that an increase of the hydrostatic pressure in A^3B^6 crystals, contrary to A^2B^6 and A^3B^5 ones, results in increasing $\varepsilon_0^{\parallel}$ component of the crystal dielectric permeability. As it was shown by direct measurements of the capacitance [26], $\varepsilon_0^{\parallel}$ of InSe in the range 10^5 to 10^9 Pa grows almost linearly by 15%. Thereof, in accord with the mean ε_0 value that in anisotropy layered crystals is defined as $\varepsilon_0 = [\varepsilon_0^{\parallel} \cdot \varepsilon_0^{\perp 2}]^{1/3}$ (where, accordingly to [18], $\varepsilon_0^{\perp} = 10.9$, $\varepsilon_0^{\parallel} = 9.9$, and indexes $\parallel$, $\perp$ correspond to parallel and perpendicular orientation relatively to the optical axis C), ε_0 grows by 5%. This ε_0 increase should result in decreasing the exciton binding energy R_0 . Indeed, the decrease of R_0 from 14.2 meV down to 12.9 ± 0.4 meV at $P = 1$ GPa was reported in [9]. The obtained in [9] R_0 value and observed in [26] ε_0 increase by 5% are in a good agreement with the well known dependence

$$R_0 [\text{meV}] = 13605 \cdot \mu / \varepsilon_0^2 \quad (7)$$

combining R_0 with ε_0 and μ - reduced exciton mass (in InSe $\mu = [m_e^{-1} + m_h^{-1}]^{-1} = 0.12m_0$ [18], where m_0 is the mass of the free electron).

Extrapolating data of [9, 26] onto our case of the van der Waals gap growth, one can say that at $x = 2$ ($P = 9.4$ MPa) ε_0 should decrease by 0.7% and R_0 increase by 0.2 meV, which at $x = 0.5$ and $\Delta\varepsilon_0(P) = 0.2\%$ results in $\Delta R_0(P) = 0.06$ meV and the respective long-wave shift of E_1 .

The performed analysis of obtained by various authors data upon the pressure influence on the energy structure of InSe crystal enables one to draw the conclusion that the short-wave shift of E_1 by 4.5 meV cannot be reasonably explained by $R_0(P)$, $\varepsilon_0(P)$ and $E_g(P)$ dependencies, as $R_0(P)$ and $E_g(P)$ contributions into this shift are opposite at $x = 0.5$ ($P = 2.4$ MPa) and their total contribution is only 0.01 meV, which is considerably lower than the observed one.

At the same time, this behaviour of exciton parameters $E_1(x)$ and $\Gamma_1(x)$ gives grounds to deem that the short-wave shift of the exciton absorption band is caused by the ε_0 increase stemming from hydrogen presence in interlayer space, which in accord with Eq. (7) results in R_0 decrease.

To make our discussion convenient, we shall describe the ε_0 increase caused by molecular hydrogen in interlayer space introducing an additive to $\varepsilon_0^{\parallel}$ parameter $\varepsilon^*(x)$ increasing with x and characterizing the degree of dielectric permeability anisotropy for the medium comprised by the exciton in the following form:

$$\varepsilon_0(x) = [\varepsilon_0^{\perp 2} \cdot \varepsilon_0^{\parallel} \cdot \varepsilon^*(x)]^{1/3} \equiv \varepsilon_0 \cdot \varepsilon^*(x)^{1/3}, \quad (8)$$

where parameter

$$\varepsilon^*(x) = \prod_{j=1}^w \varepsilon_j(x) \equiv \varepsilon_i(x)^w. \quad (9)$$

w is the degree index characterizing the quantity of interlayer space comprised by the exciton diameter d_{exc} , and $\varepsilon_i(x)$ is the depended on x dielectric permeability of the van-der-Waals gap, which is equal to that of vacuum $\varepsilon_i(0) = \varepsilon_v = 1$ in the case of pure InSe.

To simplify our estimation procedure, we shall consider that hydrogen introduction into interlayer space changes neither E_g nor μ . Then, the short-wave shift of $E_1(x)$ in the range $0 < x = 0.5$ (see Fig. 3c) is caused by R_0 decrease from 14.5 down to 10.0 meV, which results in practically linear growth of the obtained experimental $\varepsilon_0(x)$ values from 10.5 to 12.6 in accord with Eq. (7) (see insert of Fig. 3b) and is described rather well by the following dependence:

$$\varepsilon_0(x) = 10.5 \cdot (1 + 1.5 \cdot x)^{1/3} \quad (10)$$

shown with the curve 2. The curve 2 in Fig. 3c represents the dependence $R_0(x)$ for $0 < x = 2$ obtained according to Eq. (7) in the case when $\varepsilon_0(x)$ corresponds to Eq. (10). As it can be seen, the curve 2 well describes the experimental dependencies $R_0(x)$ in the range $0 < x = 0.5$. In accord with Eq. (8), $\varepsilon_0^{\parallel}(x)$ increases from 9.9 up to

16.9 due to the growth of parameter $\varepsilon^*(x)$ from $\varepsilon_v = 1$ up to 1.7. In accordance with the expression

$$a_{\text{exc}} [\text{nm}] = 0.053 \cdot \varepsilon_0(x) / \mu, \quad (11)$$

where a_{exc} is the exciton radius the exciton diameter grows linearly with changing $\varepsilon_0(x)$ from 9.51 up to 11.43 nm, which is equivalent to the increase of the exciton diameter from $d_{\text{exc}} = 11.3$ up to 13.5 crystal layers (layer thickness of InSe $d_{\text{layer}} = 8.44 \text{ \AA}$). Thereof, for $w = 13$ in agreement with Eq. (9) at $x = 0.5$ ($P = 2.3 \text{ MPa}$) and $T = 80 \text{ K}$, one can deduce $\varepsilon_i = 1.04$.

Considering Eq. (10) defining the dependence of ε_0 on x , which is associated with hydrogen introduction into interlayer space, we may perform extrapolation of $\varepsilon_0(x)$ to $x = 1$. Obtained data will be as follows: $\varepsilon_0 = 14.25$ and parameter $\varepsilon^* = 2.5$. R_0 should decrease down to 6.45 meV, while the exciton diameter should increase to $d_{\text{exc}} = 12.9 \text{ nm}$ ($d_{\text{exc}} = 15.3$ crystal layers). For $w = 15$ at $x = 1$ ($P = 4.7 \text{ MPa}$) and $T = 80 \text{ K}$, one can determine $\varepsilon_i = 1.062$.

In the similar way, for $x = 2$ we can obtain $\varepsilon_0 = 16.67$ and $\varepsilon^* = 4.0$, $R_0 = 5.73 \text{ meV}$, $d_{\text{exc}} = 15.1 \text{ nm}$ ($d_{\text{exc}} = 17.9$ crystal layers). For $w = 18$ at $x = 2$ ($P = 9.4 \text{ MPa}$) and $T = 80 \text{ K}$, one can determine $\varepsilon_i = 1.081$. It is clear seen that ε_i value also grows with x and begins to approach to experimental data inherent to the dielectric permeability of condensed hydrogen [15], which is 1.253 and 1.230 at the temperature 14K and 20.5K, respectively.

The obtained numeric values for dependencies of parameter ε^* and ε_i on x are well described by the following analytical expressions:

$$\varepsilon^*(x) = \varepsilon_v + 1.5 \cdot x \quad (12)$$

and

$$\varepsilon_i(x) = \varepsilon_v + 0.06 \cdot x^{1/2}, \quad (13)$$

where $\varepsilon_v = 1$. It is seen that ε_i growth causes increasing the crystal dielectric permeability as a whole, which leads to the experimentally observed R_0 decrease in full accordance with Eqs. (7) and (10), as shown by curve 1 in Fig. 3c.

However, at $0.5 < x < 1$, $E_1(x)$ shift changes its sign by the opposite one, and at $1 < x < 2$ E_1 position is stabilized. This behaviour of $E_1(x)$ allows us to posit that $\varepsilon_i(x)$ increase causes a growth of a_{exc} . As a consequence, parameter $\varepsilon^*(x)$ characterizing the degree of anisotropy inherent to medium comprised by the exciton grows so much that at $\varepsilon^* = 1.7$ ($x = 0.5$) the exciton motion is localized in the plane of layers. Further increase of $\varepsilon_i(x)$ increase causes reducing the exciton radius and quantum well width d_{QW} . This concept is confirmed by the experimental data for $\Delta E_1(x)$ that are shown with open circles in the insert of Fig. 3c. These experimental data are rather well approximated by the following dependence:

$$\Delta E_1(x) [\text{meV}] = 13 / \exp[x/2 \cdot (x - 0.5)] \quad (14)$$

represented by the curve 3 in this figure. The total $E_1(x)$ dependence taking into account the increase of the medium dielectric permeability and exciton localization in the crystal layer plane is depicted by the curve E_g .

In Fig. 3d shown with squares is the dependence of the localized exciton quantum well width on the parameter $\varepsilon^*(x)$ obtained in accordance with Eq. (1) and experimental $\Delta E_1(x)$ data. For convenience, we chose the thickness of the crystal layer as a unit of the d_{QW} . Open circles show the dependence of the exciton diameter d_{exc} on parameter $\varepsilon^*(x)$ without taking into account exciton localization, while solid circles do that considering the localization in the QW.

As seen from this figure, in the range of parameter values $1 < \varepsilon^*(x) < 1.7$ the QW does not appear ($d_{QW} = \infty$), and we deal with the ordinary growth of d_{exc} (open circles) bound with $\varepsilon_i(x)$ increase. At $1.7 < \varepsilon^*(x) < 2.5$, strong localization of the exciton takes place in the layer plane, and the QW narrows from 107 down to 12.8 layers. At the same time, d_{exc} decreases from 13.5 down to 8.8 layers.

Further x increase, in accord with Eq. (12), causes $\varepsilon^*(x)$ parameter growth from 2.5 up to 4.0 and decrease the QW and exciton diameter down to $d_{QW} = 12.8$ layers and $d_{exc} = 10.55$ layers. R_0 and d_{exc} are stabilized the final level, and the exciton is localized in the crystal layer plane. Experimental data of $d_{QW}(\varepsilon^*)$, where [see Eq. (12)] $\varepsilon^* = f(x)$, is well approximated by the following expression:

$$d_{QW}(\varepsilon^*) \text{ [layers]} = 9 + 0.4/(\varepsilon^*(x) - 1.7)^3 \quad (15)$$

represented by the curve 1 in Fig. 3d.

Note that numeric d_{exc} values at $\varepsilon^*(x) > 1.7$ were obtained in approximation that increasing the parameter up to $\varepsilon^*(x) > 1.7$ should be followed by the condition $\varepsilon_i(x)^w \leq 1.7$. As $\varepsilon_i(x)$ value grows with x , the quantity of layers comprised by the exciton w should be decreased.

This statement is confirmed by the experimental dependence of the half-width of $n = 1$ exciton absorption band Γ_l on x depicted in Fig. 3b. Indeed, the experimentally observed d_{exc} growth in the range $x < 0.5$ results in increasing probability of exciton scattering by point defects and increasing the initial value of homogeneous broadening the ground as well as excited exciton states $\Gamma'_l(0) = g^2 [\hbar \Omega R_0 / i^2 - \hbar \Omega]^2$. Despite the more smooth $\Gamma_l^2(T)$ dependence, the total exciton scattering rises at low temperatures ($T = 80K$), which results in experimentally observed Γ_l growth. In the range $x > 0.5$, the exciton localization causes $\varepsilon_i(x)$ growth and d_{exc} decrease, which results in stabilization of exciton and quantum well sizes and reaching a stationary value of the probability for excitons to be scattered by defects. The experimental $\Gamma_l(x)$ dependence is in accordance with Eq. (6) depicted by the curve 1. Here $\Gamma_l = 4.4$ meV.

Comparing InSe with GaSe crystals show that in GaSe crystals described above phenomena of E_1 nonlinear behaviour with x are less expressed and more delayed on large hydrogen concentration. The main reason of these differences is that in GaSe crystal exciton diameter ($d_{exc} = 9$ crystal layers) is less, then in InSe crystal, where exciton diameter d_{exc} envelop 11.3 crystal layers. It is clear that at smaller exciton diameter the described phenomena require larger hydrogen concentration. That is why in H_x GaSe crystals the effects of reduction of exciton

binding energy and subsequent exciton localization with increasing of hydrogen in van der Waals gap are more delayed and much less expressed.

Oneself paid attention that for $T = 80\text{K}$ and $x = 0$ the experimental half-width of $n = 1$ exciton absorption band - Γ_1 in InSe crystals is greater than in GaSe crystals. First of all it is connected with that fact that in GaSe crystals the energy of homopolar phonon is essentially higher than in InSe crystals and hence its contribution to Γ_1 broadening as well as to growth of integral intensity of $n = 1$ exciton absorption band up to classical values is manifested at a higher temperatures.

One can say that the obtained by us experimental results upon 2D exciton localization (taking place due to the growth of the crystal dielectric permeability anisotropy parameter) with $\varepsilon_0^{\parallel}$ are very close to [27] where the behaviour of polaron excitons in parabolic quantum dots were considered and shown that the dot size decrease results in increasing the exciton binding energy.

4. Conclusions

Conducted investigations of hydrogen intercalation in layered InSe and GaSe crystals shown that hydrogen in atomic state enter in van der Waals gap and forms H_2 molecules which with the growth of hydrogen concentrations up to $x = 2$ have a tendency to occupy translation ordered states in the gap and causes there a pressure resulting in experimentally observed and predicted by our calculations growing interlayer lattice parameter C_0 . It was established, that the preliminary irradiation by the laser beam with $\lambda = 1.06\mu\text{m}$ increase a speed of hydrogen intercalation in these crystals.

At $x = 2$ and $T < 80\text{K}$ this state of H_2 in the gap can be treated as “quazy-liquid monolayer”. At temperatures of liquid helium molecular hydrogen in the van der Waals gap and layer crystal forms a supperlattice consisting from a layered crystal lattice and a lattice of molecular hydrogen cryocrystal built in its van-der-Waals gap. At $x > 2$ atomic hydrogen begins to incorporate into interstices of the crystal lattice due to quantum-size effects arise in the gap and strong repulsion of between H_2 molecules.

Besides the growth of interlayer lattice parameter C_0 a growth of a layer lattice constant a_0 with hydrogen concentration is also observed. It was connected with incorporation of hydrogen into interstices of the crystal lattice.

It was found that the observed at $T = 80\text{K}$ non-monotonic shift of the $n = 1$ exciton absorption band peak with x stems from the increasing dielectric permeability ε_0 of the crystal due to presence of H_2 molecules in the gap. A growth of exciton anisotropy parameter $\varepsilon^*(x)$ results in decrease of the exciton binding energy R_0 . When $\varepsilon^*(x)$ exceed critical value $\varepsilon^* \leq 2$, 2D localization of exciton motion in the crystal layer plane followed by growth of R_0 takes place, which causes, reduction and then stabilization of sizes both for the exciton and quantum well. Due to difference in exciton diameter ($d_{\text{exc}}^{\text{GaSe}} < d_{\text{exc}}^{\text{InSe}}$) this phenomena in GaSe crystals are more delayed and much less expressed.

Deintercalation of hydrogen from H_xInSe and H_xGaSe crystals was carried out for 3÷9 hours at $T = 110^\circ\text{C}$ using permanent pumping out. Degree of their deintercalation increases linearly from 60% at $x \rightarrow 0$ up to 80-85 % at $x \rightarrow 4$. The

further investigation of intercalation-deintercalation processes of a given crystal powders with size of grains about $5\div 20\text{ }\mu\text{m}$ have shown that the concentration of hydrogen can easily reached $x = 6$ and degree of deintercalation achieved values up to 90 %. Repeated cycles of hydrogen intercalation-deintercalation do not result in essential worsening of physical parameters of InSe and GaSe crystals.

Conducted investigation shown that layered InSe and GaSe crystals and their powders can be considered and may be applied as working elements for solid state hydrogen storage.

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INTERACTION OF Mg-REM-Ni ALLOYS AND COMPOSITES WITH HYDROGEN

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Abstract. The alloys with low grain sizes were determined to have the best hydrogenation kinetics. The additives of intermetallide $\text{La}(\text{Mm})\text{Ni}_5$ were found to enhance the rate of hydrogen uptake and to decrease the temperature of dehydrogenation.

Keywords: Alloy; Composite; Hydrogen; Intermetallide; Ternary eutectic; Hydrogenation kinetics; Mechanochemical treatment; Hydrogen sorption.

1. Introduction

Magnesium ternary eutectic alloys (having contents 70–75 wt. % Mg – 6–9 wt. % (La)Mm – 19–21 wt. % Ni) are of great interest as hydrogen storage materials. These alloys consist of Mg, Mg_2Ni and $\text{Ln}_2\text{Mg}_{17}$ phases and are able to absorb up to 5.4–5.8 wt. % of H_2 at 520–550K and 1.0–1.5 MPa. Hydrogen releases from formed hydride phases at 610–620K and 0.15–0.20 MPa while hydrogen sorption characteristics being not changed essentially after multiple cycles hydrogenation–dehydrogenation [1, 2].

The goal of the present work was to study the interaction of ternary eutectic magnesium alloys (72% Mg – 8% La – 20% Ni, 72% Mg – 8 % Mm – 20% Ni) with hydrogen in details as well as to study the effect of intermetallide $\text{La}_{1-x}\text{Mm}_x\text{Ni}_5$ additives on the kinetics of hydrogenation of the magnesium alloy.

2. Experimental

For preparation of alloys nickel by cleanliness of 99.99 %, magnesium by cleanliness of 99.95 %, lanthanum by cleanliness of 99.79 %, and mishmetall (industrial mixture of rare-earth metals (REM): Ce – 50, La – 27, Nd – 16, Pr – 5, others REM – 2wt. %) were used. The melting of metal charge was carried out in the vacuum-induction furnace under fluxing agent from eutectic melt LiCl–KCl. The composition of alloys was supervised by the chemical analysis and the X-ray testing.

The X-ray analysis of initial alloys and products of their interaction with hydrogen was spent on an automatic complex consisting from diffractometer ADP-1 (Cu K_{α} -emission) and the managing computer. The error of definition of parameters of crystal lattices did not exceed 0.0004 nm for initial alloys and 0.0007 nm for products of their reactions with hydrogen.

Preliminary activation of alloys and their hydrogenation was carried out in laboratory installation of high pressure on techniques [3]. The composition of hydride phases formed at interaction with hydrogen was expected on size of change of pressure in the calibrated system and was specified by a standard method of burning of a sample in a current of oxygen. The equilibrium in systems alloy–hydrogen was studied by a method of construction of isotherms "dissociation pressure – composition of hydride phase" [3]. As a source of high-pure hydrogen was used the metal-hydride accumulator of hydrogen designed by us [4].

Crushing of alloys before and after processing by hydrogen was spent in an atmosphere of hydrogen or argon on planetary spherical mill (capacity of drums on 100 ml, maximal acceleration of grinding balls 700 m/s², spherical loading – relation of weights of spheres to weight of a sample – from 1:1 up to 50:1, time of crushing from 0.2 till 24 hours).

All work with samples was carried out in an atmosphere of argon.

3. Results and Discussion

Hydrogenation was performed at hydrogen pressure of 1.5–5 MPa and temperatures of 473–573 K. It was found that the first cycle of hydrogenation was completed much more faster if the alloys were grounded down to the particle size less than 200 μm and the alloys having less grain sizes were hydrogenated faster than the ones of coarse grains. The interaction of the alloy 72% Mg – 8 % Mm(La) – 20% Ni with hydrogen produces a mixture of 3 hydride phases: MgH_2 , Mm(La)H_3 and Mg_2NiH_4 , with the intermetallic compound $\text{Mm(La)}_2\text{Mg}_{17}$ being decomposed to form MgH_2 , and Mm(La)H_3 .

Repetition of the cycles "sorption H_2 – desorption H_2 " reduces the particle sizes of the alloy, after 5 cycles 90% of powdered sample have the particle sizes 20–100 μm .

The desorption isotherms of the systems (Mg–La–Ni) – H_2 and (Mg–Mm–Ni) – H_2 clearly demonstrate 2 plateaus at temperatures of 573–673K, which are correspond to the phase transitions in the systems $\text{Mg}_2\text{Ni} - \text{H}_2$ and $\text{Mg} - \text{H}_2$ with the heat of hydride formation of -70 and -75 kJ/mol respectively.

Optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) data obtained from the surface of metallographic section of initial alloy were compared with those from the surface subjected to hydrogen

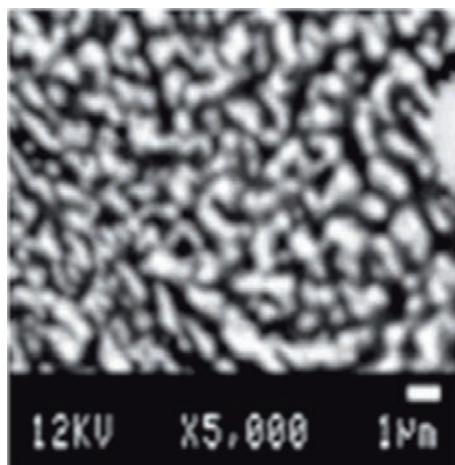


Figure 1. SEM image of the surface of a compact piece of the initial alloy.

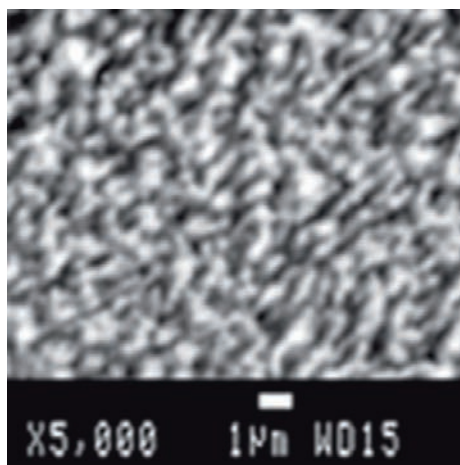


Figure 2. SEM image of the surface of a compact piece of the alloy after hydrogenation.

impact during 1 h at 573 K and 3 MPa of H_2 . This comparison evidences noticeable changes in the surface structure (Fig. 1–2).

At low degree of hydrogenation of the alloy the XRD images show the absence of the lines corresponding to the phase La_2Mg_{17} as well as the presence of the ones of lanthanum hydride phase. However the lines of the phases MgH_2 and Mg_2NiH_4 are not observed (Fig. 3). One may assume that at the initial stage of hydrogenation the hydrogenolysis of the phase La_2Mg_{17} takes place, the reaction proceeding to a considerable depth from the surface of a compact piece. It seems to be due to the hydrogen diffusion rate through grains and interphase boundaries is much higher than that through grains their selves.

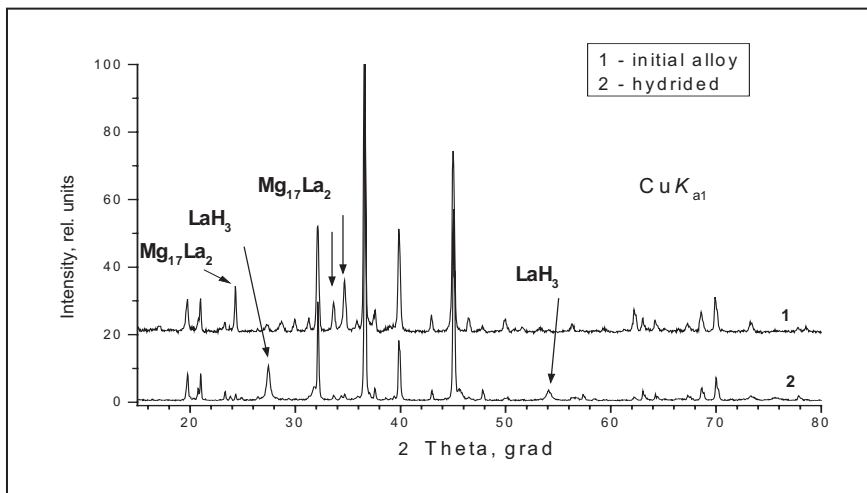


Figure 3. X-ray diffraction data of the surface of a compact piece of the alloy before and after hydrogenation.

The comparison of optical microscopy (Fig. 4) and SEM (Figs. 1–2) images for both surfaces evidence a decrease in grain sizes under the hydrogenation, that may confirm decomposition of one of the phases during the initial hydrogenation stage.

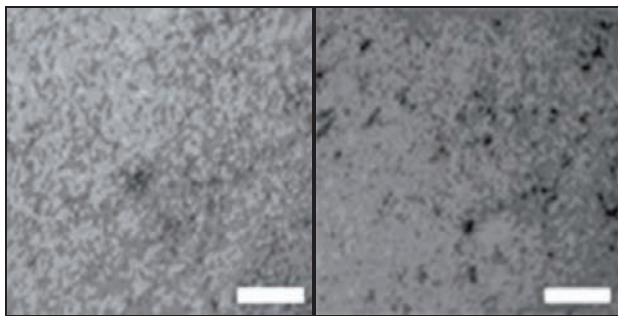


Figure 4. Images of the initial (left) and hydrogenated surface of the alloy (scale bar is 10 μm).

The mixtures of hydrogenated alloys Mg-Mm(La)-Ni and La(Mm)Ni_5 were mechanochemically treated to prepare hydrogen storage composites with various content ratios. The performed investigations demonstrate the homogeneity of the composites, the absence of new phases and the composites having particle sizes of 10–80 μm .

The hydrogenation and dehydrogenation processes of the obtained composites were studied. These composites were found to interact with hydrogen much faster than initial mixtures of the powders. The desorption isotherms (Fig. 5) obtained at temperatures 523–573 K demonstrate 2 plateaus, which are correspond to the phase transitions in the systems $\text{Mg}_2\text{Ni-H}_2$ and Mg-H_2 (isotherms for the systems $\text{La(Mm)Ni}_5\text{-H}_2$ and La(Mm)-H_2 are not revealed because of their small quantity).

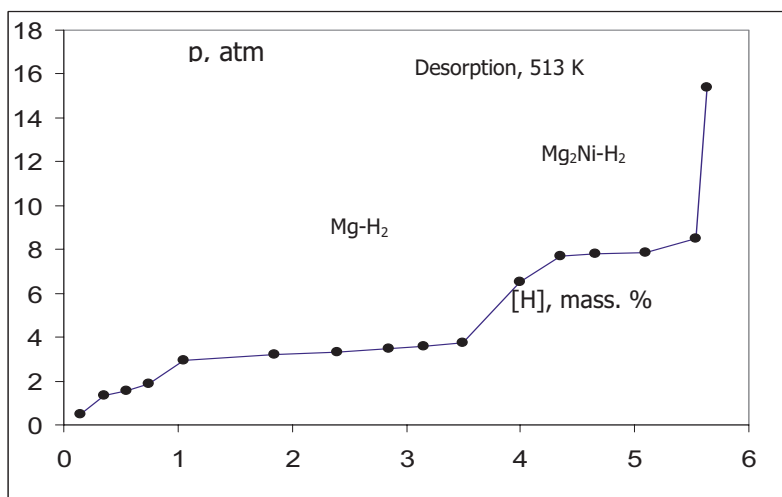


Figure 5. Desorption isotherms in the system $\{\text{Mg-Mm(La)-Ni} + 2\% \text{ La(Mm)Ni}_5\} - \text{H}_2$.

It was found that the hydrogenation rate of the composites was determined by the heat transfer rate, the hydrogen sorption capacity was about 5 wt. %. The capacity is stable after multiple cycles of "sorption-desorption H_2 ".

Acknowledgment

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CALORIMETRIC INVESTIGATION OF HYDROGEN INTERACTION WITH ZrMn_2

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Abstract. The interaction of hydrogen with ZrMn_2 Laves phase compound at pressure up to 60 atm and temperature range from 100 to 305 °C has been investigated using reaction calorimetry. The obtained results allow us to propose the existence of two hydride phase in the $\text{ZrMn}_2\text{-H}_2$ system.

Keywords: Intermetallic Compounds (IMC); Hydrides; Calorimetry; $\text{ZrMn}_2\text{-H}_2$ system.

1. Introduction

Intermetallic compound (IMC) ZrMn_2 with the hexagonal C 14 structure, belonging to Laves phase, is the forefather of the large family of AB_2 -type IMC, which is applied as materials for hydrogen storage and transportation. There are a lot of works devoted to study of ZrMn_2 structure, hydrogen storage capacity and thermodynamic parameters of $\text{ZrMn}_2 - \text{H}_2$ system. But in these works thermodynamic properties were studied in terms of van'Hoff plots, which suggest temperature independence of partial molar enthalpy (ΔH) of hydrogen reaction with ZrMn_2 . The studies of $\text{ZrMn}_2 - \text{H}_2$ system, carried out by means of calorimetric method, are significantly less and the data for changes of partial molar enthalpy of reaction ZrMn_2 with hydrogen are practically absent.

2. Experimental

The ZrMn_2 was prepared by arc melting from the pure components in the arc-furnace with tungsten nonconsumable electrode on a copper water cooled heart under purified argon pressure 1-1,5 atm. All starting materials had purity better 99.99%. For the additional purification of argon from oxygen and nitrogen the zircon getter was melted before starting smelting procedure. An excess amount of Mn was added (4 wt.%) to compensate of weight loss during melting. The buttons of the melted alloy were turned over and remelted four times to ensure homogeneity. The sample was annealed at 950°C for 10 days in the sealed quartz in vacuo. To prevent an interaction of the sample material with quartz it was put into tantalum container.

The crystal structures of the starting alloy and its hydride were characterized by $\text{Cu K}\alpha$ X-ray diffraction using Thermo Ariel diffractometer. The Rietveld refinement of diffraction profiles was performed in RIETAN '97 program. An accuracy of determination of the cell parameters was $\pm 0.001 - 0.005 \text{ \AA}$.

To prevent the hydride of ZrMn_2 from burning since it was a very fine powder, a vessel with tested hydride was cooled in liquid nitrogen, slowly opened to air and

then filled with hexsan. This treatment led to a poisoning of the centers of hydrogen recombination that reduced kinetics of dehydriding reaction.

XRD results for ZrMn_2 and its hydride confirmed the presence of C 14 structure as a major phase and ZrO_2 as minor phase. X-ray diffraction pattern of starting alloy is shown in Fig. 1. The lattice parameters of the hexagonal C 14-type structure were refined to $a=5.031 \text{ \AA}$ and $c=8.261 \text{ \AA}$ and they are in good agreement with the reference data [1-5]. The hydrogenation of ZrMn_2 did not change its crystal structure type but led to an expansion of its unit sell volume about 20%. The chemical composition of alloy and its homogeneity were examined by electron microscopy and electron probe analysis.

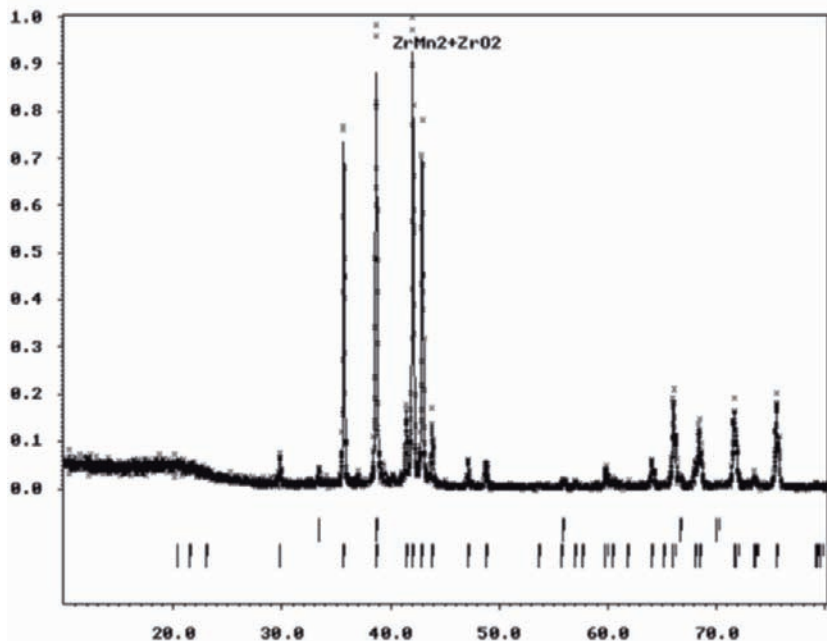


Figure 1. Cu K α diffraction pattern for ZrMn_2 .

For the measurements of the dependences of differential partial molar enthalpy of absorption and desorption (ΔH_{abs} and ΔH_{des}) and equilibrium hydrogen pressure (P) on hydrogen concentration in ZrMn_2 and on temperature of reactions of hydriding and dehydriding, twin-cell differential heat-conducting calorimeter of Tian-Calvet type connected to apparatus for gas dosed feeding was used. The apparatus scheme was described elsewhere [6]. The mass of testing ZrMn_2 alloy was 1.8996g.

3. Results and Discussion

The $\text{ZrMn}_2\text{-H}_2$ system was studied in the wide temperature range from 100 to 305°C and hydrogen pressure up to 60 atm. The advantage of the calorimetric method, applied in the present work, is the possibility to obtain calorimetric data simultaneously with P-C isotherms (P -equilibrium pressure, $C= [\text{H}]/[\text{ZrMn}_2]$).

The hydrogen desorption P-C isotherms measured at selected temperatures (100, 170, 245 and 305°C) and the absorption isotherm at 245°C for the ZrMn_2 are plotted in Fig. 2.

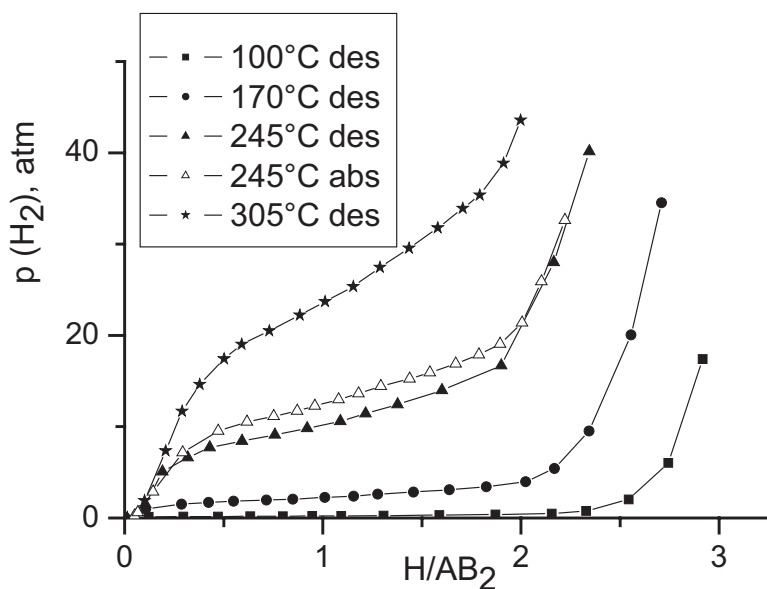


Figure 2. Absorption and desorption isotherms for the ZrMn_2 - H_2 system.

As could be seen from Fig. 2 the sloping plateaus in the two-phase region are a typical features of the ZrMn_2 - H_2 system, moreover the slope of these plateaus increase with rising of the experimental temperature and the region of two-phase equilibrium is shortened. Further it should be marked the presence of pressure hysteresis within plateau region. The value of this hysteresis at 245°C is equal ≈ 2.5 atm, the dissipation of the free energy at hysteresis $RT \ln(P_{\text{abs.}}/P_{\text{des.}}) = 0.88 \text{ kJ/moleH}_2$ where $P_{\text{abs.}}$ and $P_{\text{des.}}$ are the plateau pressure for absorption and desorption processes, respectively. Earlier [7] it has been found that the ZrMn_2 - H_2 system has large isothermal pressure hysteresis equal to 7.18 kJ/moleH_2 at 50°C. This value is in a good agreement with present data since it is well known that the magnitude of hysteresis decreases with rising of temperature.

Now let turn to an examination of the obtained calorimetric data presented in Figs. 3-6 and in sequence to analyze the changes of differential partial molar enthalpy depending on hydrogen concentration in the IMC and experimental temperature.

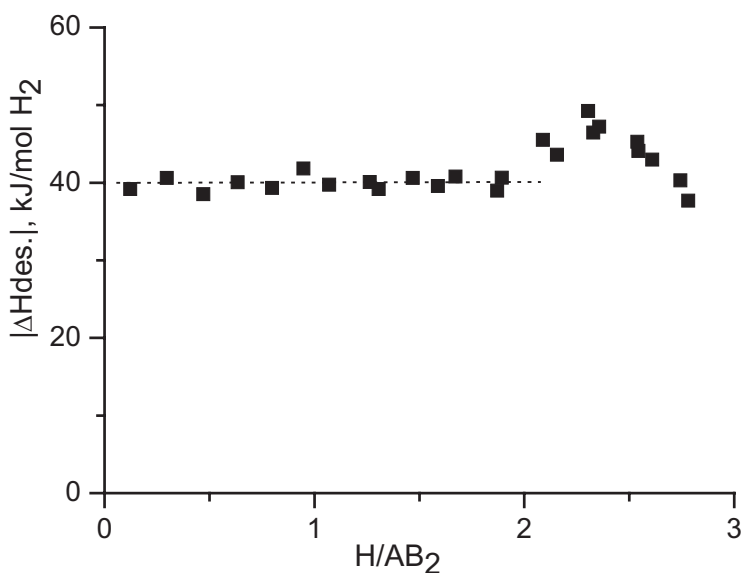


Figure 3. Desorption enthalpy vs. composition at 100°C.

Figure 3 presents the plot of the desorption enthalpy as a function of hydrogen concentration at 100°C. Since at 100 °C in the $\text{ZrMn}_2\text{-H}_2$ system there is an initial region ($C < 0.125$) where hydrogen pressures are negligibly small for the pressure gauge used here we could not obtain the P-C isotherm and the calorimetric data for the region of α -solid solution hydrogen in IMC. The values of $|\Delta H_{\text{des}}|$ in the region of the $\alpha \leftrightarrow \beta$ - transition ($C < 2.0$) are constant and equal to 39.9 ± 0.9 kJ/mole H_2 . It corresponds with the reference data good enough, namely, Flanagan and co-worker [8] obtained $|\Delta H_{\text{des}}| = 37.4$ kJ/mole H_2 at 50°C and $[\text{H}]/[\text{ZrMn}_2] = 1.5$ (that corresponds to the middle of the two-phase region), and Magomedbekov [9] gave the average values of $|\Delta H_{\text{des}}| = 42.5$ kJ/mole H_2 at the middle of the plateau. A special attention should be paid to the range $2.0 < C < 3.0$ on the plot of the $|\Delta H_{\text{des}}|$ -C dependence which is accepted to be considered as the region of the hydrogen dissolution into β -phase. As it could be seen in Fig. 3 when hydrogen is removed from the single-phase hydride region the $|\Delta H_{\text{des}}|$ values increase and pass through a maximum (to $|\Delta H_{\text{des}}| \approx 50$ kJ/mole H_2) and then continuously decrease down to the values of $|\Delta H_{\text{des}}|_{\text{plat}}$. Previously the same dependence has been marked in the works of Magomedbekov [9] and Flanagan [8]. The significant increase in the values of desorption enthalpy on the boundary $\beta/\alpha + \beta$ (≈ 10 kJ/mole H_2) the authors of both works attributed to the fact that crystal lattice of hydride phase has continued to preserve the parameters β -phase for same time when a decomposition of hydride started. It is interesting to note, that Flanagan and co-workers [8] studied $\text{ZrMn}_{2-x}\text{H}_y$ ($x = -0.2, 0, 0.5$ and 1.0) and the same $|\Delta H_{\text{des}}|$ -C dependences were observed for all researched IMC, but the most length this phenomenon had in case of ZrMn_2 (~ 1 $[\text{H}]/[\text{ZrMn}_2]$).

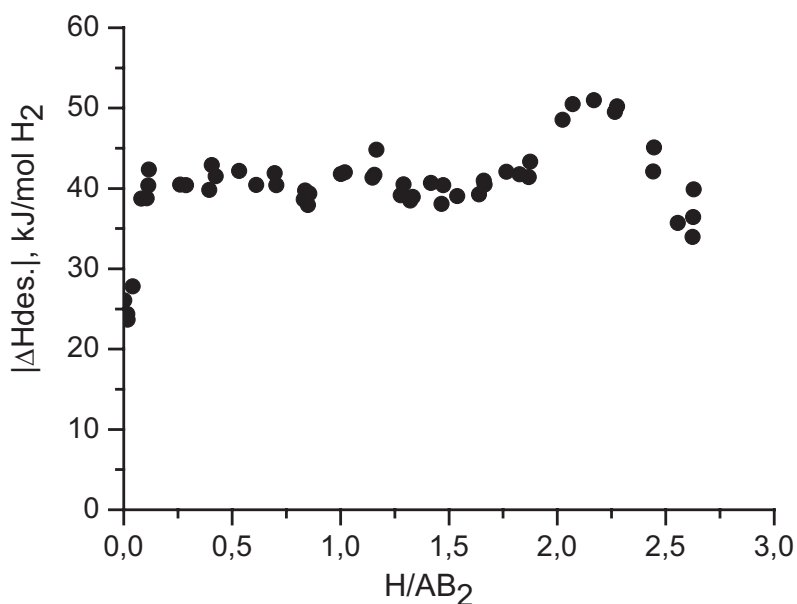


Figure 4. Desorption enthalpy vs. composition at 170°.

With rising of the experimental temperature from 100°C to 170°C the plot of the $|\Delta H_{des.}|$ -C dependence changes its shape (see Fig. 4). In the α -solid solution region of hydrogen in IMC the values of desorption enthalpy $|\Delta H_{des.}|$ increase from 24.2 kJ/mole H_2 to 43.3 kJ/mole H_2 (~ 20 kJ/mol H_2). In comparison with the plot for 100°C the $|\Delta H_{des.}|$ values in the two-phase region ($0.2 < C < 1.8$) do not remain constant over the plateau range, but the function $|\Delta H_{des.}| = f(C)$ acquires more complex character. The plateau range can be divided into two parts: $0.2 < C < 1.1$ and $1.1 < C < 1.8$. Earlier it has been established [10-12] that hydrogen atoms in the $ZrMn_2$ compound with hexagonal Laves phase structure mainly occupy tetrahedral interstitial sites $24(l)$, $12(k)_1$, $6(h)_1$ and $6(h)_2$. It could be supposed, that when rising temperature hydrogen atoms relocate between occupied sites and the difference in the energy of hydrogen interaction with different metal atoms forming these interstitial sites becomes more noticeable so that calorimetric measurements carried out in the wide temperature range permitted us to notice it. Previously it has been found for $TiMn_{1.5}D_3$ [13] that relocation of hydrogen atoms takes place at -193°C ($\sim 0.25D$) and in the work [14] for $(Ti_{0.9}Zr_{0.1})(Mn_{0.75}V_{0.15}Ti_{0.1})_2D_{2.8}$ the authors recognized that at low temperature (-256°C) approximately 0.11 deuterium atoms relocate from the $24(l)$ to the $12(k)_1$ position. Since both compounds are classified as AB_2 -type IMC with hexagonal Laves phase structure and they are compositionally similar to $ZrMn_2$ then our assumption expressed above may be correct.

The transition between two states of hydride phase takes place at the composition $ZrMn_2H_{1.1}$. On the P-C diagram at 170°C (see Fig. 2) a small fold in

the range of concentration $[H]/[ZrMn_2] \sim 1.1$ could be seen. The position of this fold agrees with the boundary between two parts on which we have divided the plot of the $|\Delta H_{des.}|$ - C dependence. On the base of these results we assumed that there are two hydride phases in the $ZrMn_2$ - H_2 system at $170^\circ C$, namely, $ZrMn_2H - \beta_1$ -hydride and $ZrMn_2H_{2+Y} - \beta_2$ -hydride. At $[H]/[ZrMn_2] > 2$ we also observed rising of the enthalpy values up to maximum magnitude (~ 50 kJ/mol H_2) corresponding to boundary $\beta_1 \leftrightarrow \beta_2/\beta_2$ and then $|\Delta H_{des.}|$ decreased in the range of the existence of β_2 -hydride.

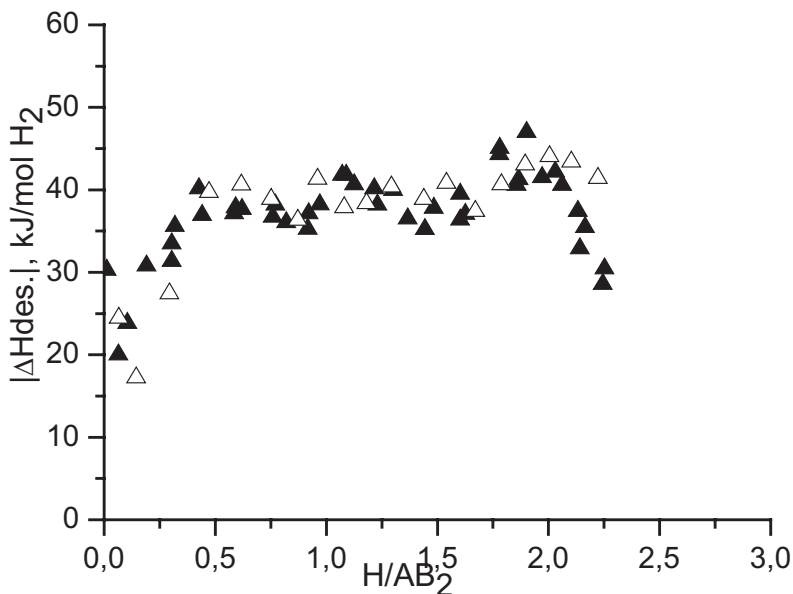


Figure 5. Absorption and desorption enthalpies vs. composition at $245^\circ C$: Δ – absorption, $\blacktriangle$ – desorption.

The change of $|\Delta H_{abs.}|$ and $|\Delta H_{des.}|$ as a function of H content at $245^\circ C$ are shown in Fig. 5. The shape of desorption isotherm $|\Delta H_{des.}|$ - C at $245^\circ C$ as one can see from Fig. 5 is similar to the isotherm $|\Delta H_{des.}|$ - C obtained for $170^\circ C$ but there are some peculiarities. The length of the α -region increased ($0 < C < 0.4$). The relative partial molar enthalpy changes in this region pass through a minimum and then rise to the values of $|\Delta H_{des.}|_{plat}$. The difference in the $|\Delta H_{des.}|_{min.}$ and $|\Delta H_{des.}|_{plat}$ values is approximately equal to 20 kJ/mole H_2 . The boundaries between two states of hydride phase at $245^\circ C$ are clearer. The boundaries of the $\alpha \leftrightarrow \beta_1$ transition may be defined as $0.4 < C < 1.0$, and $\beta_1 \leftrightarrow \beta_2$ transition as $1.0 < C < 1.8$. It should be noted that at $245^\circ C$ the values of the relative partial molar enthalpy does not remain constant, namely, at $C \approx 0.4$ $|\Delta H_{des.}| \approx 40$ kJ/mole H_2 and at $C \approx 1.0$ $|\Delta H_{des.}| \approx 35$ kJ/mole H_2 . The same dependence is observed for the range $1.0 < C < 1.8$: the lower value of H concentration corresponds to the higher value of $|\Delta H_{des.}|$ and the upper value of H concentration corresponds to the lower of $|\Delta H_{des.}|$ (see $C \approx 1.0$

$|\Delta H_{des.}| \approx 40 \text{ kJ/mole H}_2$, $C \approx 1.8$ ($|\Delta H_{des.}| \approx 35 \text{ kJ/mole H}_2$). One could see on the $|\Delta H_{des.}|$ - C isotherm at 245°C in the range of high H concentration that there is a wide maximum ($1.8 < C < 2.5$) where the magnitudes of $|\Delta H_{des.}|$ reach $\sim 50 \text{ kJ/mole H}_2$ and then slowly decrease. The similar maxima were observed for $|\Delta H_{des.}|$ - C dependences measured at 100 and 170°C .

As mentioned above for 245°C the hydrogen absorption isotherm was obtained (see Fig. 2 and Fig. 5). Comparing the absorption and desorption isotherms one could see that hysteresis of the enthalpy values is absent in practice even for the range of H concentrations $1.8 < C < 2.5$ for which in reference data [8, 9] $|\Delta H_{des.}| > |\Delta H_{abs.}|$.

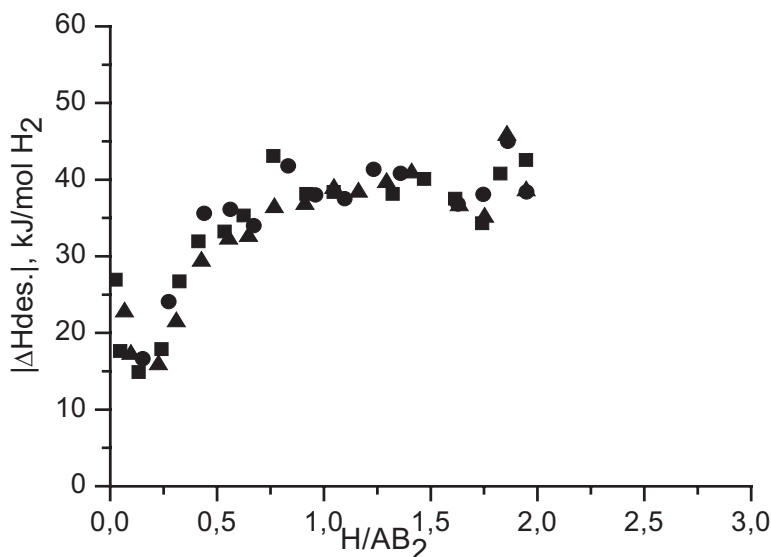


Figure 6. Desorption enthalpy vs. composition at 305°C .

As seen from Fig. 6 at 305°C the values of partial molar enthalpy for different runs of hydrogen desorption have a large deviation probably because of a proximity to critical temperature, thus it is difficult to determine the phase boundaries. The critical temperature for the existence of ZrMn_2 hydride phase estimated by different authors is 277 – 327°C [8] and 318°C [15]. The plot of the $|\Delta H_{des.}|$ - C could be divided into three parts: the hydrogen α -solid solution region ($0 < C < 0.6$), $\alpha \leftrightarrow \beta_1$ transition ($0.6 < C < 1.0$) and $\beta_1 \leftrightarrow \beta_2$ transition ($1.0 < C < 1.8$).

The presence of minimum in the $|\Delta H_{des.}|$ - C dependences in the α -solid solution region is typical for the ZrMn_2 - H_2 system. The magnitude of this minimum is about 20 kJ/mole H_2 , and it coincides with references data [8]. Flanagan and co-workers [8] explained this phenomenon by the presence of trapping sites in ZrMn_2 , e.g. interstices surrounded by 3 Zr and 1 Mn rather than the usual occupied interstices with 2 Zr and 2 Mn atoms.

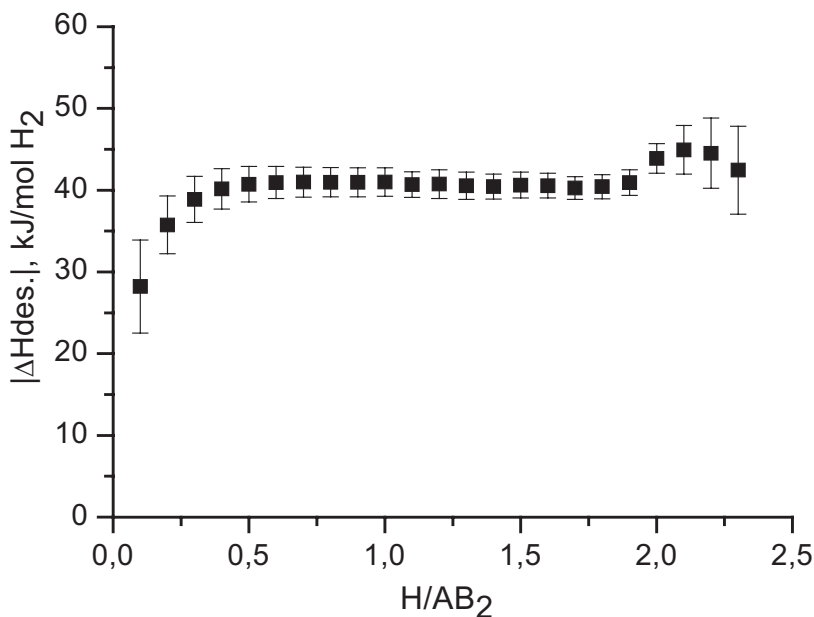


Figure 7. Partial molar desorption enthalpy calculated from van't Hoff plot.

The relative partial molar enthalpy changes for hydrogen desorption were calculated from the van't Hoff plots based on the measured P-C-T relations. The obtained $|\Delta H_{des.}|$ -C dependence was plotted in Fig. 7. The shape of this plot is similar to one obtained for 100°C in this work and those presented in [8, 9] for 50°C. In this plot one can select the α -solid solution region of hydrogen in the $ZrMn_2$ -H₂ system ($0 < C < 0.5$), the plateau region ($0.5 < C < 1.8$) and the region of the single hydride phase ($C > 1.8$). In the plateau region the plot has some slopping. The values of the desorption enthalpy in the plateau range equal to $40 \div 41$ kJ/moleH₂ and they slowly decrease with increasing H concentration, that is in good agreement with calorimetric results, obtained in present work, and reference data [8, 9]. Comparing $|\Delta H_{des.}|$ -C dependences obtained via calorimetric method and plotting of pressure-composition isotherms it should be noted that calorimetric method permits better to understand the processes taking place in the studied system.

4. Conclusions

1. Hydrogen interaction with $ZrMn_2$ has been studied via calorimetric and P-C isotherm methods at 100, 170, 245 and 305°C.
2. It has been established that in the $ZrMn_2$ -H₂ system the partial molar enthalpy of hydrogen reaction with $ZrMn_2$ changed with the temperature of experiment and hydrogen concentration in this system. The obtained data allow us to

suppose that these changes are connected with the order of filling of tetrahedral interstitial sites by hydrogen in the metal matrix, that have different facing, and to make an assumption that two hydride phases are formed.

3. We did not observed hysteresis in the values of the absorption and desorption enthalpies at 245°C. At this temperature $|\Delta H_{\text{abs}}|$ is equal to $|\Delta H_{\text{des}}|$ over the range of hydrogen concentrations. It should be recognized that for a further investigation of a region with high hydrogen concentration in the $\text{ZrMn}_2\text{-H}_2$ system is needed.

Acknowledgments

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STRUCTURE OF NbVCoD_{2.5} SYNTHESIZED UNDER HIGH GASEOUS PRESSURE

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Abstract. Under high pressure of hydrogen (up to 200 MPa) has been synthesized deuteride of intermetallic compound NbVCo with hexagonal Laves phases structure. Maximum content of hydrogen was determined with thermodesorption method and corresponded composition NbVCoD_{2.5}. The position of hydrogen and metallic atoms and occupation of the sites have been determined by X-ray and neutron powder diffraction. Have been demonstrated that V and Co atoms statistically distributed in sublattice of B-component (2a, 6h sites) and hydrogen atoms mainly occupied 24l and 12k sites, typically hydrogen sites in hexagonal Laves phases.

Keywords: Laves phases, NbVCoD_{2.5}, high gaseous pressure of hydrogen, neutron diffraction

1. Introduction

AB₂ intermetallic compounds (IMC) with Laves phases structure are reversible absorbents of considerable amount of hydrogen and are interesting as potential hydrogen storage materials [1]. Experimental [2] and theoretical [3] investigation revealed, that maximum hydrogen content in these intermetallic compounds corresponds 6,0-6,5 atom at formula unit in case, when compounds contents hydrogen forming elements. IMC ZrVCo is typical example of such compound, crystallized in C14 structure type (hexagonal Laves phases) and easy absorbs under low pressure (up to 10 MPa) hydrogen until AB₂H_{3,3} composition [4]. At the same time, intermetallic compound NbVCo with the same structure and slight less cell volume (at 10%) doesn't interact with hydrogen under usual conditions according [5]. The goal of the present work is to synthesize of NbVCo hydride under high pressure (up to 200 MPa) and make structural analyses with X-ray and neutron powder diffraction.

2. Experimental

The starting alloy NbVCo was melted from pure metals by using electrical furnace under inert atmosphere and quenched in evacuated quartz ampoule at 800°C temperature during 240 hours. Hydride was synthesized at high pressure apparatus [6]. After synthesis sample of hydride was transferred into passive state by cooling to liquid nitrogen temperature and left at this temperature in air during one hour.

Amount of absorbed hydrogen was checked by thermodesorption method. All samples were analyzed by powder X-ray diffraction using a «ThermoARL» diffractometer ($\lambda_{Cu}=1.5406 \text{ \AA}$). Neutron data were obtained on «DISK» diffractometer at the «Kurchatov Science Centre». Deuterium rather than hydrogen has been used in order to reduce the incoherent scattering. Obtained results were refined with «Fullprof» and «Rietan» programs.

3. Conclusions

X-ray analyses have been shown that the sample NbVCo is single phase and has C14 structural type with cell parameters (table 1) corresponding references [7]. Specific nature of IMC NbVCo is that X-ray make weak difference between V and Co atoms with the close atomic numbers and for neutron V atoms are invisible. Using both methods allowed to determine (table 2,3; Fig. 1,2) that in NbVCo Nb atoms located in 4f site (site of A atoms in AB₂) and V and Co atoms distributed in accordance with composition in 2a, 6h - B site in the hexagonal structure of Laves phase.

TABLE 1. X-ray and neutron diffraction data of NbVCo and NbVCoD_{2.5}

Compositi on	Structural type	Cell parameters			
		a, Å	c, Å	V, Å ³	ΔV/V, %
X-ray data					
NbVCo	MgZn ₂	4.932(2)	8.03(1)	169	-
NbVCoD _{2.5}	MgZn ₂	5.129(2)	8.38(3)	191	13.0
Neutron data					
NbVCo	MgZn ₂	4.916(2)	8.03(2)	168	-
NbVCoD _{2.5}	MgZn ₂	5.129(2)	8.36(2)	190	13.1

TABLE 2. Structural data of X-ray diffraction for NbVCo and NbVCoD_{2.5}

Atom	Site	Number of atoms in elementary cell	Coordinates		
			x	y	z
NbVCo					
Nb	4f	4.00(2)	0.333	0.666	0.064(2)
Co1	2a	0.98(3)	0	0	0
V1	2a	1.01(3)	0	0	0
Co2	6h	3.00(2)	0.830(2)	0.660(2)	0.25
V2	6h	2.88(2)	0.830(2)	0.660(2)	0.25
Rp=9.7%, Rw=7.5%					
NbVCoD _{2.5}					
Nb	4f	4.00(3)	0.333	0.666	0.067(3)
Co1	2a	1.20(3)	0	0	0
V1	2a	1.08(2)	0	0	0
Co2	6h	2.82(1)	0.831(2)	0.662(2)	0.25
V2	6h	2.94(2)	0.831(2)	0.662(2)	0.25
Rp=9.4%, Rw=8.6%					

TABLE 3. Structural data of neutron diffraction for NbVCo deutride

Atom	Site	Number of atoms in elementary cell	Coordinates		
			x	y	z
Nb	4f	4.00(1)	0.333	0.666	0.087(3)
Co1	2a	0.90(2)	0	0	0
V1	2a	1.02(3)	0	0	0
Co2	6h	3.30(1)	0.833(1)	0.666(1)	0.25
V2	6h	2.94(1)	0.833(1)	0.666(1)	0.25
D1	24l	6.48(2)	0.026(2)	0.338(3)	0.549(3)
D2	12k ₂	1.68(1)	0.410(2)	0.820(2)	0.610(3)
D3	6h ₁	0.48(3)	0.429(2)	0.858(2)	0.25
D4	6h ₂	0.36(2)	0.201(2)	0.402(2)	0.25
Rp=10.4%, Rw=9.5%, R _B =13.7%, Nb _{4.00} V _{3.96} Co _{4.20} D _{9.00}					

I/I₀

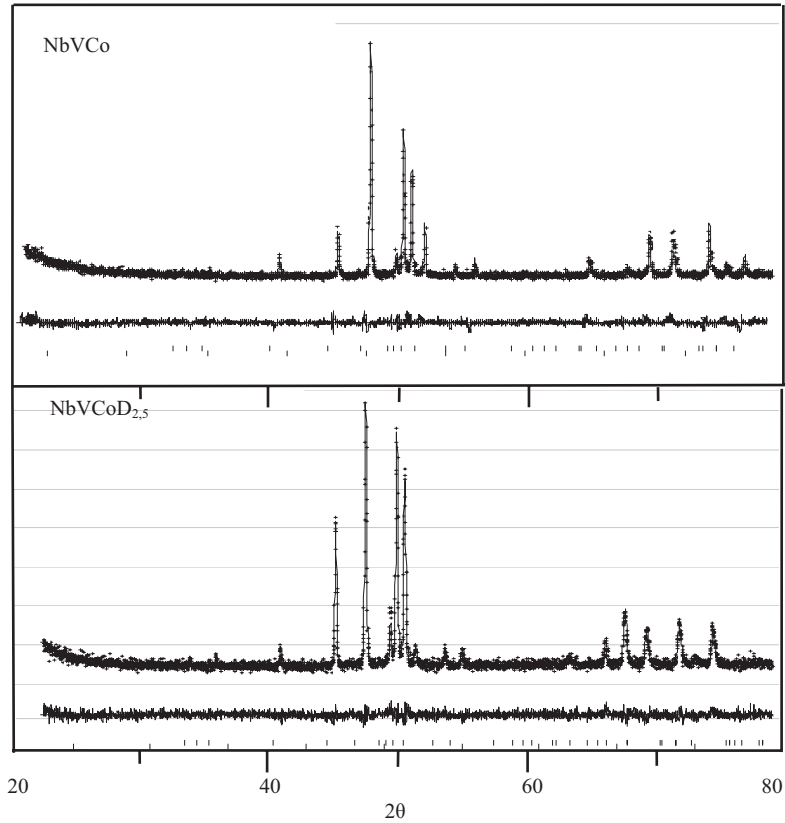
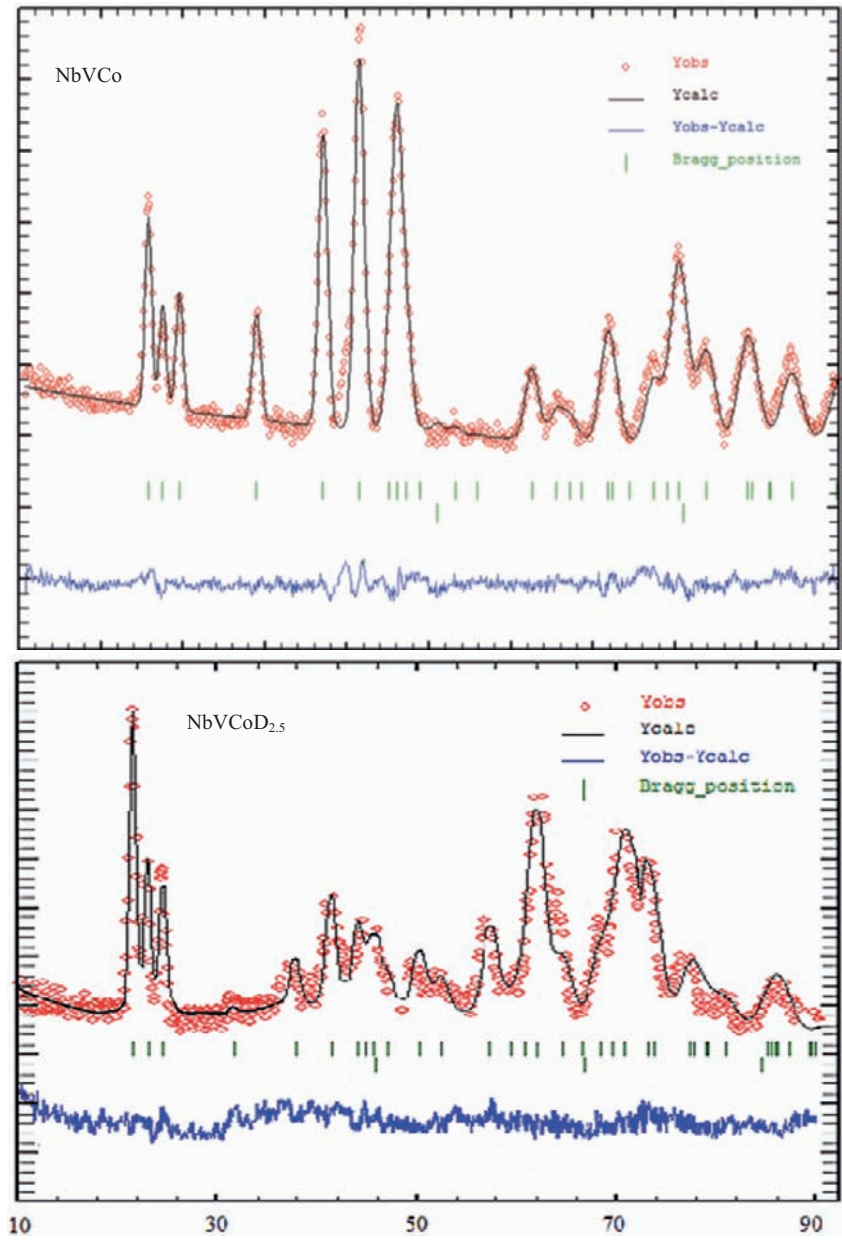


Figure 1. X-ray diffraction patterns of NbVCo and NbVCoD_{2.5}.

I/I_0



2θ

Figure 2. Neutron powder diffraction patterns of NbVCo and NbVCoD_{2.5}.

Sample of hydride, obtained under high pressure with maximum contents NbVCoD_{2.5}, has been kept at liquid nitrogen temperature, than was reloaded quickly into special cryostat for neutron investigation and has been studied at low and room temperatures. Cooled samples for X-ray investigations have been studied at room temperatures and during heating process. X-ray and neutron data have been revealed small decreasing hydrogen contents in NbVCoD_{2.25} as heating result and father decreasing hydrogen until NbVCoD_{2.05} after long leaving at room temperature.

In accordance with calculations have been established, that in solid solution hydrogen occupied all sites with A₂B₂ coordination, typical for Laves phases (l, k, h₁, h₂), but with different probability (table 4). Generally hydrogen atoms occupied l and k sites (in rate 4:1), and in h site the occupancy is less than one atom at elementary cell of hydride (0,84) and this occupancy decreasing until 0,6 with lowering of the hydrogen content.

TABLE 4. Atomic distances in NbVCoD_{2.5}

Atom	d, Å	Atom	d, Å	Atom	d, Å
Nb-Nb	3.12	Co-V	2.56	D ₁ ¹ -D ₁ ⁴	1.69*
Nb-Co	3.00	V-V	2.57	D ₁ ¹ -D ₂ ²	1.80*
Nb-V	3.01	D ₁ ¹ -D ₁ ²	0.85*	D ₁ ¹ -D ₁ ³	1.99**
Co-Co	2.57	D ₁ ¹ -D ₂ ¹	1.02*	D ₂ ¹ -D ₂ ²	2.30

Blocked sites: *fully, **particularly.

Obtained results have been shown that is clearly preference of the tetrahedral sites (A₂B₂) occupancy with hydrogen (24l > 12k₂ > 6h₁ > 6h₂). This circumstance was noted early for hydrides based on ZrVCo in [4], where was revealed analogues situation. Part of hydrogen atoms, located in the weak occupied sites 6h is small – about one atom at elementary cell. This portion of atoms is slightly dependents of temperature and is determined obviously as rejection of hydride composition from stoichiometry (AB₂D₂ for NbVCo and AB₂D₃ for ZrVCo). Portion of superstoichiometrical atoms (about one atom at elementary cell) approximately corresponds the number of 6h occupied sites. So, is possible to expect that with exactly stoichiometry will be occupied only 24l and 12k₂ sites. In C14 hexagonal lattice around each A atom is possible to allocate a slight distorted hexagon, consisting of k, l, h₁ and h₂ sites (Fig. 3). Here we consider a possible occupancy of these sites with hydrogen in the framework of blocking interstices model, developed as for binary hydrides [8,9] and for hydrides of IMC [2,10]. This model corresponds of consideration of the nearest order in position of introduced atoms such way that probability of site occupancy with hydrogen atom, closest to the occupied site, is small or equal zero. According of the experimental data the blocking radius (R₀) in different hydrides is hesitated about medium size 2,0 Å in diapasons 1,8-2,2 Å. This radius is necessary to compare with (k-l) and (h-h) site distances in hexagons (table 4,5; Fig. 3), which depend from lattice positional parameters of IMC and change with increasing of hydrogen concentration. If occupancy these hexagons with hydrogen were equally (without blocking), the part of k-site in (k-l) hexagon would be determinate by number of Wyckoff position and would correspond ½. If a blocking radius of l site is more than distance until

A₂B₂). In the complex lattice, unlike of simple solid solution, the idea of stoichiometry becomes more complex. It determined now as not a simple rate of a number of interstitial sites to a number of metallic atoms like in binary hydrides, but rate of a number of metallic atoms ranges to a number of hydrogen hexagon considering of different sites number and hydrogen average concentration in hexagon (for example AB₂(D₁^lD₃^k)_x).

TABLE 5. Atomic distances in ZrVCoD_{3.3} [4]

Atom	d, Å	Atom	d, Å	Atom	d, Å
Zr-Zr	3.31	Co-V	2.73	D ₁ ¹ -D ₁ ⁴	1.83*
Zr-Co	3.16	V-V	2.73	D ₁ ¹ -D ₂ ²	2.04**
Zr-V	3.17	D ₁ ¹ -D ₂ ¹	1.14*	D ₁ ¹ -D ₁ ³	2.17
Co-Co	2.61	D ₁ ¹ -D ₁ ²	1.15*	D ₂ ¹ -D ₂ ²	2.49

Blocked sites: *fully, **particularly.

At present work has been established forming hydride with maximum content NbVCoD_{2.5} under high gaseous pressure. The structure of the hydride has been analyzed with X-ray and neutron powder diffraction and has been shown that hydride is the solid solution hydrogen in intermetallic compound. Have been revealed that hydrogen atoms occupied preferably l and k sites in the lattice and superstoichiometrical atoms located in h-sites. The explanation of preferably character of the hydrogen different sites occupation have been given on base of the idea of blocking sites, closest to hydrogen occupied inside of hexagon range.

Acknowledgements

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STRUCTURAL AND METHODICAL FEATURES OF THE INSTALLATION FOR INVESTIGATIONS OF HYDROGEN-SORPTION CHARACTERISTICS OF CARBON NANOMATERIALS AND THEIR COMPOSITES

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Abstract. The laboratory setup for investigations of hydrogen capacity of materials has been created at the Institute for Problems of Materials Science of NAS of Ukraine. It completely meets the modern requirements for the experimental equipment of this class. The setup design makes it possible to investigate hydrogen-sorption characteristics of different materials with low specific density, including nanocarbon structures and composites on their basis, by the volumetric method in the pressure range between 0.01 and 16 MPa H₂ and at temperatures from 77 K to 1273 K. The setup provides a sufficient degree of accuracy. It is equipped with a metal-hydride unit for hydrogen storage/compression. The design and service conditions of this device are discussed.

Keywords: metal-hydride, fullerene, carbon nanofiber and nanotube, hydrogen, sorption, volumetric measurement.

1. Introduction

Currently increasing deficit of hydrocarbon fuels caused by depletion of their natural resources is responsible for instability in the advancement of the world economics. In addition, ecological problems related to the harmful effluents from burning hydrocarbon fuels gain momentum and become a global problem. Therefore the interest in using hydrogen as universal synthetic fuel and energy carrier both for stationary and mobile applications has been intensified worldwide. Such an approach for solving problems of our civilization is conditioned by plenum sources of raw materials for hydrogen production, high energy capacity of hydrogen, technological flexibility and safe processes of energy conversion using hydrogen with respect to environment.

Hydrogen is the lightest of known substances and therefore certain difficulties appear in solving problems of its storage in small containers. At the same time, the value of specific energy capacity of hydrogen per unit weight is much higher compared to the other natural or synthetic fuels and in its utilization environmental pollution is minimum. The chief drawback of hydrogen is too low specific energy

capacity per unit volume because in the normal conditions hydrogen is in a gaseous state and has very low boiling and critical points. At the room temperature and atmospheric pressure one gram of gaseous hydrogen occupies 11 liters and an electric car with fuel cells should store about 33000 l of gaseous hydrogen that provide 100 km run [1]. Hence the development of effective methods for compact hydrogen storage is a key problem of its use.

A successful solution of this problem should be based on the reliable experimental data. Therefore, before creating an experimental setup and developing a procedure for performing hydrogen-sorption studies, authors have made thorough and fundamental analysis of methods for hydrogen storage including in metal-hydrides and carbon nanomaterials. The analysis has revealed peculiarities and defined the main technical parameters and conditions which the modern-day experimental setup for measurements of hydrogen-sorption characteristics of carbon materials must fully meet.

2. Carbon nanomaterials as a hydrogen storage

In recent years we are pinning our hopes on carbon nanomaterials, such as fullerenes, carbon nanofibers and carbon nanotubes for the use as hydrogen-accumulating matrixes.

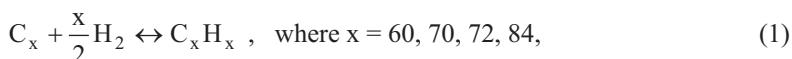
Since the discovery of fullerenes the scientific community has been taking an active interest in peculiarities of the fullerene formation and structure, physical and chemical properties. The fourth allotropic modification of carbon (fullerene) is unique molecule having a spatial structure with icosahedral symmetry and showing distinctive properties in interaction with other substances. Under certain conditions fullerenes can accept and donate hydrogen atoms to form hydrofullerenes.

Peculiarity of the fullerene molecule formation also reveals itself in a fullerite crystal structure. Cubic crystal lattices of fullerites and hydrofullerites behave like those of different metals and alloys. Fullerene molecules are distributed in the lattice sites while atoms of elements are distributed in the octa- and tetrahedral interstitial sites forming the interstitial solid solutions. Fullerene molecules substitute each other in the sites of lattice and form the substitution solid solutions. Forming exo- and endocompounds, fullerene molecules that are in the lattice sites can change considerably the properties of crystal, whereas its crystalline structure remain unchanged.

Researchers all over the world have concentrated attention to the unusual hydrogen-sorption behavior of fullerenes [2-10]. Theoretically, the prospects for application of the new materials as a hydrogen storage are sufficiently optimistic. In the case when one hydrogen atom is added to each carbon atom (what is quite possible), there appears a possibility to prepare a sorbing matrix based on these materials. The matrix allows the accumulation of 7.7 wt. % of hydrogen.

This index meets and exceeds the requirements for this class of materials (DOE, Energy Departments, USA [11] and requirements of other international organizations).

Therefore a search for the method of conducting the reversible and complete reaction



with consideration for peculiarities in the structure and properties of the materials would allow their use as sorbents to accumulate and store hydrogen in many fields of engineering and technology. As it is known, the absence of this class of materials retards a wide application of hydrogen as a universal fuel and an energy carrier.

Other carbon nanomaterials, such as single-wall carbon nanotubes (SWNT), graphite nanofibers (GNF) and their modifications doped with metals are reasonably promising for hydrogen accumulation. The generalized results on hydrogen-sorption capacity of SWNTs and GNFs (Table 1) point to that fact [12]. For clearness and analysis the data on hydrogen store in metal-hydrides (MH) [13-18] are given in the Table 1.

TABLE 1. Hydrogen-sorption characteristics of different carbon nanomaterials and metal-hydrides (MH)

Material	Maximum capacity, wt. %	T, K	P _{H₂} , MPa
“Low-temperature” MH (293–373 K)	$\frac{1.5-1.8^*}{0.8-1.3}$	293–373	0.001–2
“High-temperature” MH (523–673 K)	$\frac{3.5-7.6}{2.5-5.6}$	523–623	0.1–2
Complex hydrides (alanates)	$\frac{4.0-5.6}{3.0-4.0}$	398–438	0.1–20
SWNT	8.25	80	7.18
SWNT	5-10	133	0.04
SWNT	4.2	300	10-12
SWNT	6.5-7	300	0.1
SWNT	1.1-5.2	293	10
SWNT	3.5	300⇔77	10
GNF	0.4	298-773	0.1
GNF	2.5	300⇔77	7

*numerator shows an ideal value, denominator presents an actual value (because of insufficient effectiveness of the storage system).

In a number of cases the amounts of hydrogen absorbed by carbon nanomaterials far exceed the values required for the mobile systems of hydrogen storage although different researchers report considerably different results on the amounts of hydrogen accumulated by these materials. The reason for this discrepancy is the absence of reliable methods of production of pure SWNTs and GNFs as well as universally accepted procedures for their characterization, as an example, by purity, a degree of "opening", diameters of nanotubes, interlayer spacing and amounts of metallic catalysts. In addition, hydrogen-sorption capacity is greatly affected by the preliminary treatment of carbon nanomaterials and the purity of hydrogen in use. For this reason the data on hydrogen sorption describe

only some particular materials and cannot be still employed to compare sorption efficiency of carbon nanomaterials of different types. The mechanism of this uniquely high hydrogen capacity of carbon nanomaterials is still elusive.

Nevertheless, as it seems to us, the high hydrogen capacity of new carbon nanomaterials is actual. In addition, it is essential that carbon nanotubes (CNTs) are inert in the environment and the heat of H_2 adsorption on CNTs is considerably lower than the heat of metal hydrides formation. This allows one to look forward to a possibility of the use of carbon nanomaterials in the actual systems for hydrogen accumulation.

The intent of the investigations currently performed in the field of creation of different compositions based on carbon nanomaterials is to moderate the processes of these materials dehydrogenation and increase hydrogen capacity of some of them.

The design of the laboratory setup proposed below allows the investigations to be made of the peculiarities of hydrogen interaction with carbon nanomaterials and their composites ($T = 77 \div 1273$ K).

3. Experimental setup for measurements of hydrogen-sorption characteristics

Traditionally, hydrogen-sorption capacity is measured volumetrically on the setups of Siverts type. This universally known method is quite precise until we operate with the samples from hydrogen-sorbing materials with certain density. If specific density is low, uncertainty of the value may contribute seriously to the error in the determination of hydrogen-sorption capacity.

The experimental setup, that was manufactured on the basis of the performed evaluative calculations and analysis of literature, is designed to investigate the hydrogen-sorption characteristics predominantly of carbon materials and composites on their base with low specific density using the volumetric method in the pressure range from 0.01 to 30 MPa H_2 and the temperatures between the boiling point of liquid nitrogen and heating up to 1273 K (Fig. 1).

Constructively, this design is a high pressure gas system consisting of distribution pipelines, a main manifold and a low pressure manifold, two buffer capacities for gas branching fault, a reactor with a heating system and a metal-hydride unit for hydrogen storage/compression (Fig. 2).

The volumes of empty reactor and of connecting systems of capillary pipelines have been carefully determined by hydrogen leak-in from the calibrated system volume, i.e. the standard deviation corresponding to the estimation error for the volume is less than ± 0.01 cm³. The volume of empty reactor with capillary pipe-lines is 9.5 cm³. Pressure control is exerted by the high (to 16 MPa) and low (to 1.6 MPa) pressure diaphragm pickups with a view to bring the working pressure to the upper limit of the range of measurement (Fig. 3). Accuracy of measurements is 0.15 %. The selected pressure pickups allow the easy integration into the control system. The temperature conditions in the reactor are assured by the furnace where the heating regime is preassigned and controlled by the precision preset temperature controller RIF-101.



Figure 1. General view of the setup for investigation of hydrogen-sorption properties.

The temperatures of the sample inside the reactor and of the heating element in the furnace are controlled by thermocouples with an accuracy of $\pm 1^\circ\text{C}$. Low-temperature measurements are performed by submersion of the reactor into the Dewar flask with liquid nitrogen ($T = 77\text{ K}$). The vacuum system has been assembled on a basis of the universal vacuum unit VUP-5.

The readings from the pickups are processed by the interface block Agilent. The investigation program is given by a computer. Scanning and data processing are performed automatically.

The 220 l metal-hydride storage/compressor has been manufactured and used for production of high purity hydrogen. It provides the controlled gas leak-in at a pressure to 16 MPa.

3.1. METAL-HYDRIDE UNIT FOR HYDROGEN STORAGE/COMPRESSION

In designing this unit a special attention has been given to the system for feeding, purifying and compressing hydrogen in use.

The laboratory metal-hydride unit (Fig. 4) for high-pure hydrogen storage/compression that has been manufactured and tested in our institute is designed to operate as a part of the new setup. The main specification to the unit is a possibility to supply hydrogen into the gas system of the setup (volume varies between 15 and 500 cm³ depending on the connected buffer vessels) under the pressure controlled in the range from 10 to 160 bar. The total required hydrogen storage capacity comprises 220 l that provides intensive experimental operation during 2 - 4 weeks without recharging the unit.

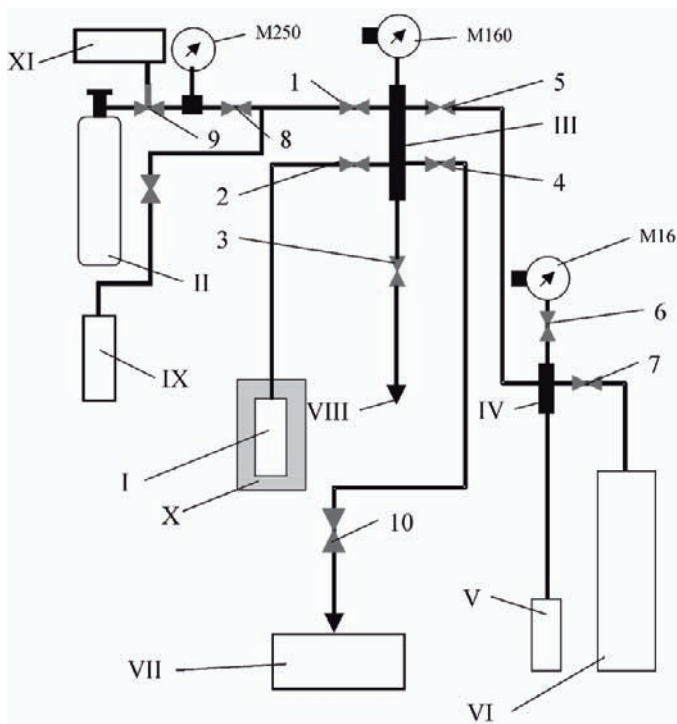


Figure 2. Gas circuit of the setup:

I - experimental reactor; II - cylinder with compressed hydrogen of technical purity, III - main collector; IV - low pressure collector; V - buffer vessel, 50 cm³; VI - buffer vessel, 300 cm³; VII - vacuum system; VIII - gas disposal line; IX - metal-hydride unit for hydrogen storage/compression, 220 l H₂; X - thermostat; XI - refueling port; M250 - high pressure indicating gauge (up to 25 MPa); M160 - high pressure diaphragm pickup (up to 16 MPa); M16 - low pressure diaphragm pickup (up to 1.6 MPa); 1-8 - hydrogen valves; 9 - hydrogen leak; 10 - vacuum valve.

3.2. DESIGN OF THE STORAGE UNIT

The container of the hydrogen storage unit (Fig. 5) is made from the tubular stainless steel case ($\varnothing 70 \times 5$ mm, $L=306$ mm) and the face flanges 10 mm in thickness. One of the flanges is a part of the internal heat exchanger made on the basis of the standard finned tube ($\varnothing 25.4 \times 2.64$ mm, $L = 295$ mm core tube, stainless steel; aluminium fins 58 mm in the external diameter and 0.4 mm in thickness, pitch of 2.3 mm). The heat exchanger has been certified by the group of Prof. Yartys V.A. at the Institute for Energy Technology (IFE) in Norway. The internal surface of the core tube is machined to allow the push fit of the standard cartridge-type electric heater ($\varnothing 20$ mm, $L=290$ mm, rated power 800 W, supply voltage 220 V). The shield for the thermocouple measuring temperature inside the intertube space is installed in the heat exchanger flange. The points for MH material loading and the fitting for gas input/output are in the opposite flange. The latter is made as a united element with a standard pipe filter (porous stainless steel, $\varnothing 11$ mm, $L=250$ mm, filter cell 5 μ m).

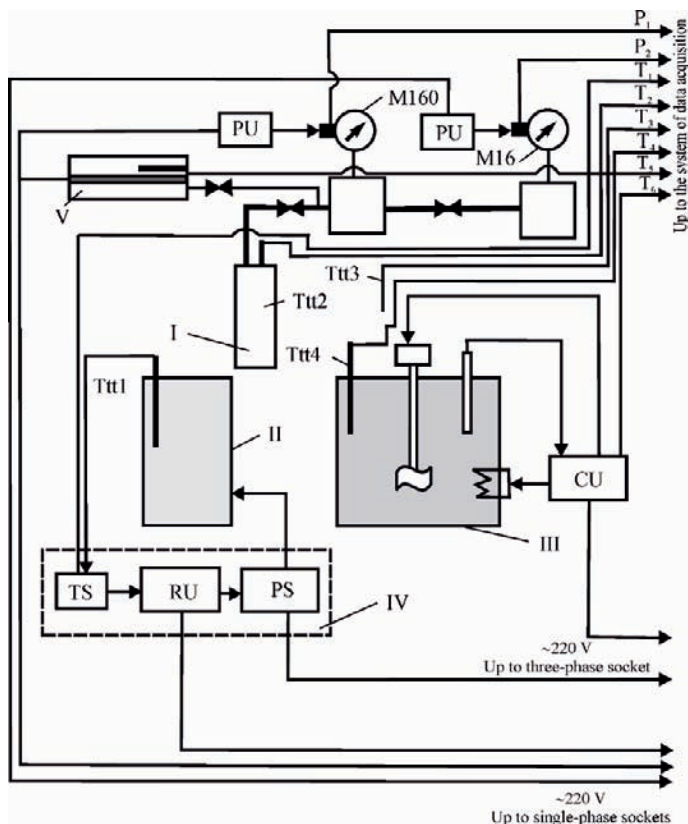


Figure 3. Measurement circuit of the setup:

I - experimental reactor; II - furnace; III - thermostat for thermostating the reactor; IV - precision preset temperature controller RIF-101; V - metal-hydride unit for hydrogen storage/compression; M160 - high pressure diaphragm pickup (up to 16 MPa); M16 - low pressure diaphragm pickup (up to 1.6 MPa); Ttt1 - Ttt6 - thermoelectric temperature transducers; PU - power unit for pressure pickup; CU - control unit of thermostat (III); TS - thermostat RIF-101 for thermostating cold ends of a thermocouple; RU - regulating unit of RIF-101; PS - power supply of RIF-101.

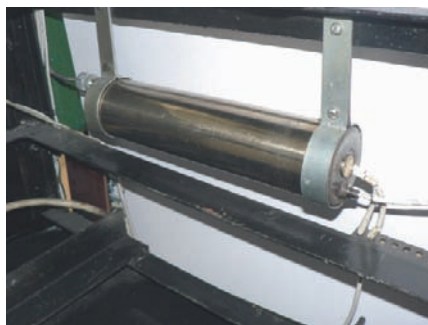


Figure 4. Position of the unit for hydrogen storage/compression in the setup.

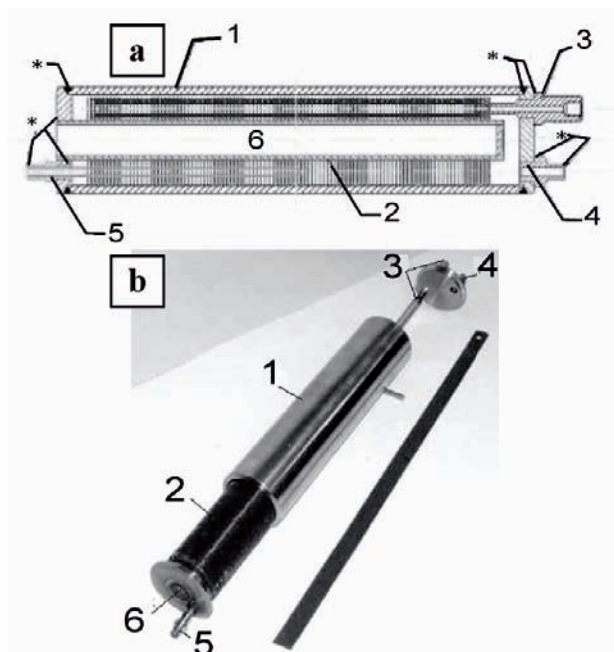


Figure 5. Assembly drawing (a) and general view before assembly (b) of M-H container: 1 - case, 2 - heat exchanger, 3 - filter with gas input/output fitting, 4 - point for metal-hydride loading, 5 - thermocouple shield, 6 - position for electric heater, * - welded seams.

According to the performed strength calculations (GOST 14249-89, safety margin 1.5, correction for the strength reduction by welding 0.8), the working pressure in the MH container can be as high as 300 bar at $T=250^{\circ}\text{C}$.

The weight of the assembled empty container is 5.2 kg.

3.3. CHOOSING THE HYDROGEN-SORBING MATERIAL

The $\text{R}(\text{Ni}, \text{Fe}, \text{Al})_5$ hydrogen storage alloy prepared on the base of the commercial cerium ligature ($\text{R} = \text{Ce}, \text{La}, \text{Pr}, \text{Nd}$), lanthanum and nickel (both of technical purity grade) has been used in the unit. The composition of the alloy must provide a hydrogen equilibrium pressure of ~ 10 bar over MH at room temperature and above 150 bar at elevated temperatures.

For this purpose the chemical composition of the working alloy that would ensure the required characteristics of the unit has been computed and selected on the basis of the literature data on the binary constitution diagrams for Ce-La, La-Ni and Ce-Ni (Figs. 6,7,8,9). The ternary diagram has been computed and constructed for the Ce-La-Ni system (Fig.10) (such diagram is unavailable in literature).

The following peculiarities have been considered in constructing the variant for a liquidus projection along the Mm-LaNi_5 section.

3.3.1. Ce-La constitution diagram

The Ce-La constitution diagram [19] is presented in Fig. 6. Thermal and microstructural analysis have revealed that δ , γ and β modifications of Ce and La form the continuous sequences of solid solutions [20, 21, 22]. The measured lattice parameters [21] have supported the conclusions that fcc polymorphous modifications of Ce and La make up the continuous sequence of solid solutions. In addition, a small deviation from Vegard's law is observed.

3.3.2. La-Ni system

Phase equilibrium in the lanthanum alloys with nickel in the range from 0 to 100 at. % Ni has been studied in [20, 23-26]. Two variants of the total constitution diagram for the La-Ni system are given in Figs. 7, 8.

The La_3Ni , LaNi , LaNi_2 , $\text{LaNi}_3 \sim \text{LaNi}_4$ and LaNi_5 compounds are formed according to the La-Ni constitution diagram described in the handbook [20]. The construction of the La-Ni constitution diagram in the concentration range between 50 and 83.3 at. % Ni was refined in the paper [25].

The six compounds as LaNi , $\text{LaNi}_{1.51}$, $\text{LaNi}_{2.286}$, LaNi_3 , La_2Ni_7 and LaNi_5 were found in the investigated concentration range. The LaNi_2 compound reported in [20, 24] does not exist in equilibrium conditions, it is a metastable phase.

Figure 7 demonstrates the La-Ni constitution diagram [23-25] in the concentration range from 50 to 83.3 at. % Ni. The part of the constitution diagram above 1100 °C and at the nickel content from 83 to 100 at. % is given according to the evidence derived from [26], and at the nickel content from 0 to 45 at. % according to [20].

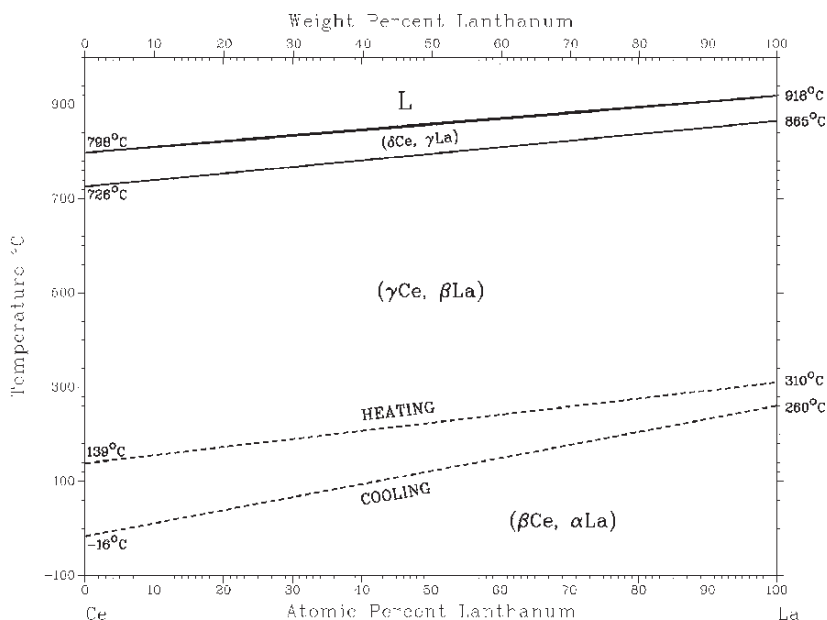


Figure 6. The constitution diagram for the Ce-La system [19].

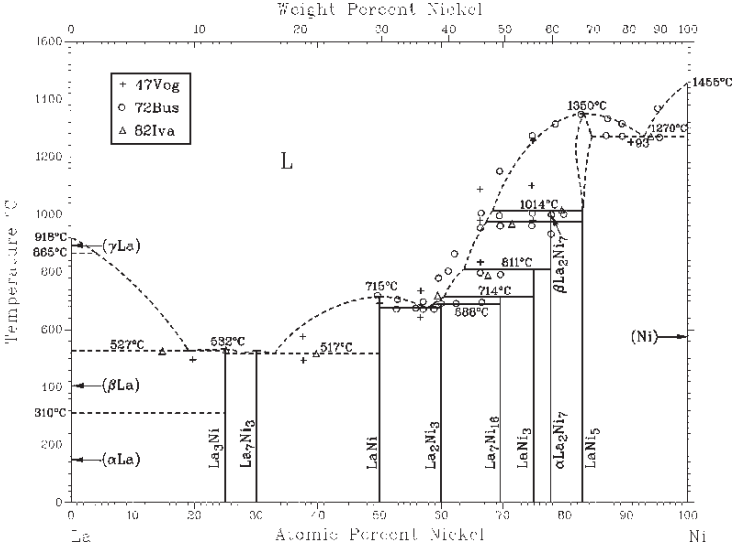


Figure 7. The constitution diagram for the La-Ni system [23-25].

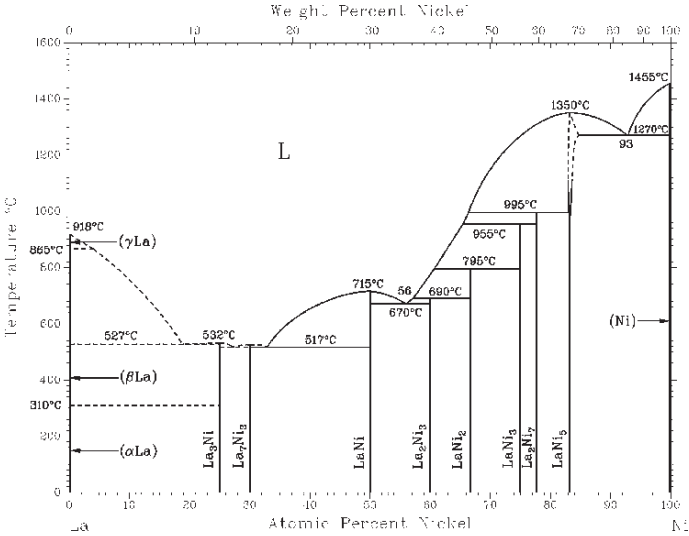


Figure 8. The constitution diagram for the La-Ni system [19].

La₃Ni, LaNi and LaNi₅ compounds are melted congruently at 532, 715 and 1350°C [26]. La₂Ni₃, La₇Ni₁₆, LaNi₃ and La₂Ni₇ compounds are formed by peritectic reactions at 688, 714, 811 and 1014°C, respectively. The La₂Ni₇ compound undergoes a polymorphous transformation at ~976°C: β La₂Ni₇ ↔ α La₂Ni₇. Four eutectics crystallize in the system:

(β La)+La₃Ni at ~527°C and ~17 at. % Ni;

La₇Ni₁₆+LaNi at 517°C and ~31 at. % Ni;

LaNi+La₂Ni₃ at 675±5°C and 57,7 at. % Ni;

$\text{LaNi}_5+(\text{Ni})$ at 1270°C and 93 at. % Ni.

La solubility in Ni was investigated in [27] and it was found to be 0.346 mass. % at 1050°C , 0.309 mass. % at 1020°C and 0.380 mass. % at 950°C .

3.3.3. Ce-Ni system

Figure 9 demonstrates the Ce-Ni constitution diagram reported in a number of papers [28-31] which summarize the results of DTA, X-ray, metallographic studies on the alloys prepared using 98-99 % pure Ce (by mass).

There exist six compounds in the system. Ce_7Ni_3 , CeNi and CeNi_5 melt congruently at 477, 495, 1210°C , respectively. The rest of the compounds are formed by peritectic reactions. The nonvariant reactions proceeding in the Ce-Ni system are given in the Table 2.

TABLE 2. Nonvariant reactions in the Ce-Ni system.

Reaction	Ni content in phases, at. %	Temperature, $^\circ\text{C}$
$\text{L} \rightleftharpoons (\gamma\text{Ce}) + \text{Ce}_7\text{Ni}_3$	18.0; ≈ 0 ; 22.0	477
$\text{L} \rightleftharpoons \text{Ce}_7\text{Ni}_3 + \text{CeNi}$	34.5; 25.0; 50.0	495
$\text{L} \rightleftharpoons \text{CeNi} + \text{CeNi}_2$	55.0; 50.0; 66.7	655
$\text{L} + \text{CeNi}_3 \rightleftharpoons \text{CeNi}_2$	62.0; 75.0; 66.7	830
$\text{L} + \text{Ce}_2\text{Ni}_7 \rightleftharpoons \text{CeNi}_3$	69.0; 77.8; 75	930
$\text{L} + \text{CeNi}_5 \rightleftharpoons \text{Ce}_2\text{Ni}_7$	72.0; 83.3; 77.8	1065
$\text{L} + \text{CeNi}_5 \rightleftharpoons (\text{Ni})$	91.0; 83.3; 99.95	1210

The reciprocal solubility of components is negligible. The Ce solubility in Ni was found to be 0.05 and 0.04 at. % at the temperatures of 1200 and 400°C , respectively [32].

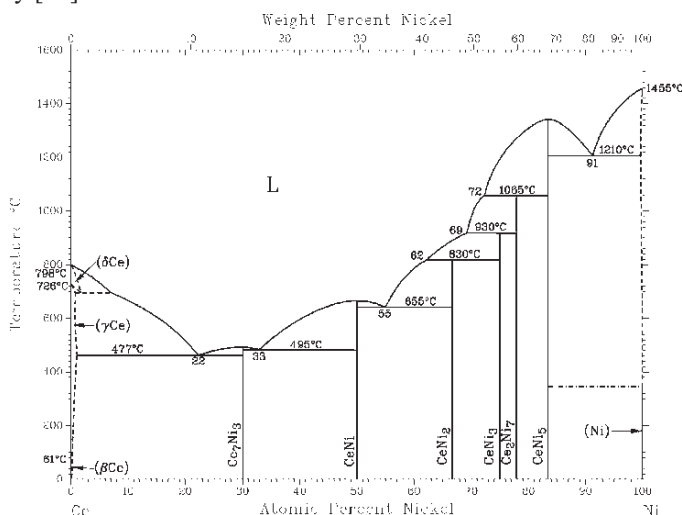


Figure 9. The constitution diagram for the Ce-Ni system [28-31].

3.3.4. *Ce-La-Ni system*

The present study of the Ce-La-Ni system has been undertaken to check the evaluated literature data and aimed at refining the position of phase boundaries in the nickel corner of the Ce-La-Ni system at melting points (crystallization of alloys). Several experimental alloys have been produced at 1-5 at. % intervals in the region rich in nickel.

The alloys have been smelted in an electric arc furnace with a permanent tungsten electrode on the copper water-cooled bottom. The bottom has holes in which the batch is alloyed from different components.

The batch is computed from the formula:

$$X \text{ (wt.\%)} = \frac{A_i M_i}{\sum_{i=1}^n A_i M_i} \cdot 100\%$$

where A_i - atomic percents of component with atomic mass M_i .

The camera has been vacuumed to $5 \cdot 10^{-2}$ mmHg (6.66 Pa) and filled with the type "A" argon to 39.9-53.3 kPa (300-400 mmHg). Additional purification of argon has been performed by melting pure titanium which served as a getter. The ingots have been turned over and remelted twice to equalize the composition of the alloy. The main smelting has been performed in the holes having the form of hemispheres. The samples have been poured into the copper mould. Melting loss of the alloys has been found to be less than 1 at. %. Starting components have been studied by the method of high-temperature differential thermal analysis (HDТА) in the temperature range from 25 to 2000 °C on the HDТА-8 unit [33].

The starting Mm consisted of 82.9 5 Ce and 16.7 % La. Chemical analysis has shown that the composition of the selected alloy after smelting corresponds to the Ce-14.51; La-17.921; Ni-67.5 (wt. %).

The weight percents have been converted into the atomic percents to obtain the formula

$$\begin{aligned} 14.51 \text{ wt.\% Ce} &= \frac{\frac{14.51}{140.12}}{\frac{14.51}{140.12} + \frac{17.92}{138.9055} + \frac{67.5}{58.71}} \cdot 100\% = 7.4915 \text{ at.\%} \\ 17.92 \text{ wt.\% La} &= \frac{0.1290}{1.3829} \cdot 100\% = 9.3282 \text{ at.\%} \\ 67.5 \text{ wt.\% Ni} &= \frac{1.1487}{1.3829} \cdot 100\% = 83.0284 \text{ at.\%} \end{aligned}$$

Hence the selected alloy corresponds to the formula $\text{Ce}_{7.5}\text{La}_{9.3}\text{Ni}_{83}$ or $\text{A}_{16.8}\text{B}_{83}$ i.e. $\rightarrow \text{AB}_{4.94}$. This suggests that the chemical composition of the alloy used in the hydrogen storage/compressor deviated of the stoichiometric composition of the AB_5 alloy to the depletion in nickel.

The cast alloys of the Ce-La-Ni system have been studied by the methods of microstructural, X-ray phase and differential thermal analyses. A fragment of the phase equilibrium diagram in the nickel corner of the Ce-La-Ni system at melting points

(crystallization) of the alloys has been constructed on a basis of the results of investigations on the cast alloys (Fig. 10).

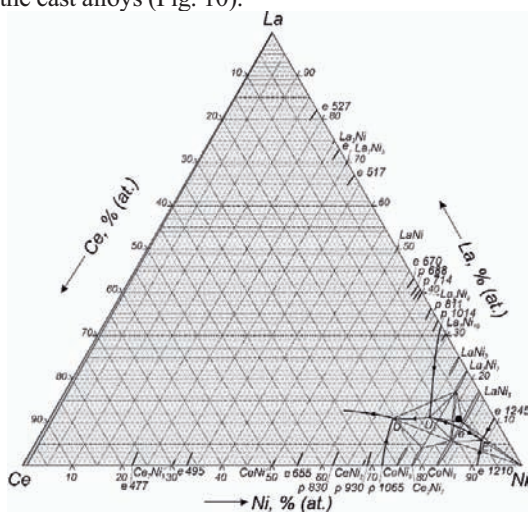


Figure 10. The phase equilibrium diagram in the nickel corner of the Ce-La-Ni system.

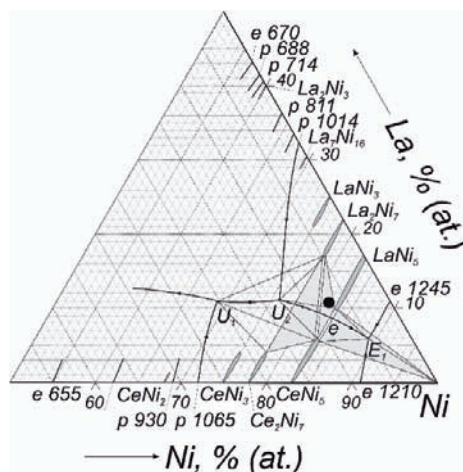


Figure 11. Fragment of the phase equilibrium diagram in the nickel corner of the Ce-La-Ni system at melting points (crystallization of alloys).

● $\text{Ce}_{7.5}\text{La}_{9.3}\text{Ni}_{83}$ alloy, at. %.

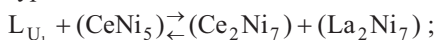
One of the selected alloys in the three-phase region has been found to be:

$(\text{LaNi}_5) + (\text{CeNi}_5) + (\text{La}_2\text{Ni}_7)$;

- the CeNi_5 and LaNi_5 phases form a quasi-binary system in which a quasi-binary eutectic exists (point e, Fig. 11);

- a three-phase eutectic (point E_1 , Fig. 11) exists in the three phase region $(\text{Ni}) + (\text{CeNi}_5) + (\text{LaNi}_5)$;

- points U_1 and U_2 in the liquidus corresponds to the other three-phase equilibrium states in the solidus. These points map the nonvariant equilibrium of a transition type:



Our alloy marked off by the black circle in the diagram is in the plane of the last nonvariant equilibrium.

At the thermal investigation of the prepared alloys the heating rate has been maintained at 30-40 D/min. Such procedure allows the registration of phase transformations in the alloys in a solid state as well as the transformations involving a liquid phase. The influence of the factors like overcooling and chemical interaction of a reactive alloy and material of a crucible on the phase transformation temperature has been also controlled. Fig. 12 demonstrates the thermal curves: (a) starting material based on mishmetal and (b) alloy of composition $\text{Ce}_{7.5}\text{La}_{9.3}\text{Ni}_{83}$ at. % used for the storage/compressor.

Three thermal effects are observed in the heating curve of initial Mm: the first one - at 595 °C, his nature is unknown, and two thermal effects at 780 °C and 810 °C. The effect at 780 °C is associated with a polymorphous transformation in pure Ce $\gamma \rightarrow \delta$ 726±5 °C, and the second one is responsible for melting pure cerium at 815 °C. Evidently the presence of the thermal effects and the difference in their temperature ranges as compared with the literature data are related to the chemical composition of starting mishmetal. Chemical analysis has shown that the base of the mishmetal is Ce 82.9 wt. % and La - 16.7 wt. %.

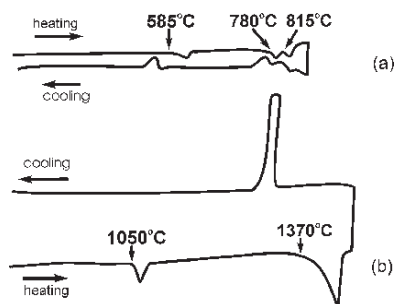


Figure 12. Thermal curves:

(a) - starting mishmetal, (b) - alloy of composition $\text{Ce}_{7.5}\text{La}_{9.3}\text{Ni}_{83}$ selected for use in the storage unit.

The presence of two thermal effects in the heating curve (Fig. 12, b) testifies that the phase composition of the alloy is shifted to the phase rich in lanthanum (see the La-Ni constitution diagram). Here the LaNi_5 compound has been melted congruently at 1340 °C, and the La_2Ni_7 compound is formed by the peritectic reaction $\text{La} + \text{LaNi}_5 \rightleftharpoons \beta\text{-La}_2\text{Ni}_7$ at 1014 °C.

Hence our metal-hydride used in the storage/compressor possesses a sufficiently homogeneous composition with an excess of rare-earth metal what

allows the hydrogen production under pressures from 0.2 to 1.0 MPa at the room temperature and up to 15-16 MPa at higher temperatures. The negligible variations in the chemical composition of the alloy can drastically change its working characteristics.

3.4. PREPARATION OF THE ALLOY FOR OPERATION

The alloy has been smelted in an electric arc furnace (mass of an ingot ~100 g).

The ingots of the alloy have been reduced to powder (particle size less than 1 mm) and loaded into the MH container. Thereupon the loading point of the container (item 4 in Fig. 5) has been welded up.

The amount of the material loaded into the container is 1.8 kg what corresponds to the filling density of 3 g/cm³.

The material has been activated directly in the container by vacuum heating up to 300 °C for 1 hour and cooling to the room temperature followed by holding in hydrogen at $P=50$ bar and cyclic heating to 200°C followed by cooling to the room temperature. The thrice-repeated replica of the last procedure has been made, the measured reversible hydrogen storage capacity of the material ($P_{H_2}=10\dots100$ bar; $T=20\dots200$ °C) reached 122 cm³/g (4.68 H/AB₅) what corresponds to the hydrogen storage capacity of the unit equal to 220 l.

3.5. RESULTS OF TESTING THE UNIT FOR HYDROGEN STORAGE/COMPRESSION

Figure 13 demonstrates a typical operation cyclogram of the unit. This example corresponds to the volume of the gas header (hydrogen collector) equal to ~100 cm³ and the residual hydrogen storage capacity in the storage equal to 130 l (60% of the maximum value).

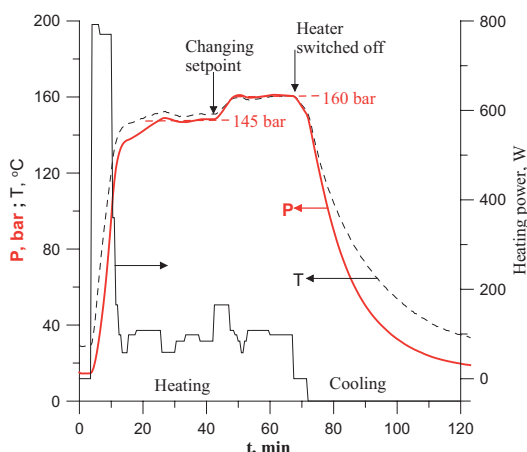


Figure 13. Typical operation cyclogram of the unit for hydrogen storage/compression.

The starting hydrogen pressure in the preliminary evacuated hydrogen header that corresponds to the equilibrium pressure of MH dissociation at room temperature (13 bar at 30 °C) is reached within 2-3 minutes. The subsequent heating of the MH container at the maximum rated power supply tends to increase the pressure up to ~90% of the set point (145 bar) in less than 10 minutes. Thereupon the pressure stabilization mode of the compressor is established. Changing the set point by 10-15% results in the transient process, 5 to 6 minutes in duration. The power consumed by the electric heater in the steady-state regime at the maximum set point (160 bar) does not exceed 100 W (12.5% of the heater rated power). In this case the maximum temperature of the MH is 150-160 °C. If the residual hydrogen storage capacity of the unit is less than 30 l and the heating power is the same, the temperature of the container substantially increases without the considerable increase in pressure and reaches to 200-250 °C at the residual hydrogen capacity of 15 l (in this case the maximum pressure is as low as 7-10 bar).

After switching-off heating and switching on the fan for the MH container cooling, hydrogen pressure drops from 160 to 50 bar in 20 minutes and to the value close to the starting one (15 bar) less than in 1 hour. The time required to set equilibrium in cooling the container can be reduced to 10-15 minutes by releasing a little amount (up to 10 l) of hydrogen gas.

Hence the designed metal-hydride unit for hydrogen storage and compression is characterized by high compactness and relatively low temperature of MH heating while the sufficiently high hydrogen pressure is generated. The unit possesses good dynamic characteristics.

4. Conclusions

The setup designed at Institute for Problems of Materials Science of NAS of Ukraine for investigations of hydrogen-sorption properties completely meets the modern requirements for the experimental equipment of this class. The setup makes it possible to investigate hydrogen-sorption characteristics of different materials including nanocarbon structures and composites on their base with low specific density by the volumetric method in the pressure and temperature range from 0.01 to 30 MPa H₂ and between 77 and 1273 K, respectively. The setup provides the sufficient degree of accuracy.

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IMPROVEMENT OF HYDRIDE HEAT DEVICES OVERALL PERFORMANCE

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Abstract. In article the analysis of an overall HHP performance from the thermodynamic and thermalphysic point of view is carried out. For perfection of HHP operation is necessary to improve hydrides, processes in hydride beds, processes heat and mass transfer in the sorbers working in consisting of HHP. The various constructive measures directed on increase of HHP efficiency are considered. It is shown that mathematical modelling can become one of fast and effective ways of HHP designing for various technical applications.

Nomenclature

Nomenclature	Enthalpy of hydride formation, (J kg ⁻¹)
ΔH	
$a = \lambda_{\text{eff}}/C_p \rho$	Factor of a temperature conductivity of a hydride bed, (m ² s ⁻¹)
C_p	Thermal capacity of a sorber (J kg ⁻¹ K ⁻¹)
C	Concentration of hydrogen, [g-atom H ₂ (mol an alloy) ⁻¹]
d	Diameter, m
G	Flow rate of the heat-carrier, (kg s ⁻¹)
K_k	Factor of a design (relation of design weight to hydride weight)
K_{hc}	Factor of a heat transfer, (W m ⁻² K ⁻¹)
P	Pressure, Pa
Q	Capacity, W
R	Gas constant, (J kg ⁻¹ K ⁻¹)
T, t	Temperature, (°C, K)
X	Relative (in weight. %) concentration of hydrogen
Fo	Fourier number
Bi	Biot number
COP	Efficiency of HHP in a refrigerator cycle as the relation of a useful cold to the spent heat
HHM, HHP	Hydride heat machine, hydride heat pump
<i>Greek symbols</i>	
α	Factor of a heat emission, (W m ⁻² K ⁻¹)
δ	Thickness of a hydride bed, a wall, m
ε	Porosity
λ_{eff}	Factor of effective heat conductivity of a hydride bed, (W m ⁻¹)

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	$K^{-1})$
ρ	Density, ($kg\ m^{-3}$)
τ	Time, s (sec)
<i>Subscripts</i>	
r	Concerns to a radial direction
a	Concerns to an axial direction, to process of hydrogen absorption
d	Concerns to process of hydrogen desorption
h, m, l	Concerns to levels of temperature: high, average, low
h	Hydride
m	Concerns to a material of a skeleton of a heat-conducting insert
ch	Characteristic
eff	Effective

Keywords: hydride, hydrogen, hydride bed, hydride sorber, hydride heat pump.

1. Introduction

Application of hydride heat machines (the HHM - the hydride heat pump (HHP), a refrigerator, a heat transformer, the compressor, the accumulator of hydrogen) is justified there where there are sources of low-potential energy or a plenty of wasted heat is not used. Systems hydrogen-metal hydrides promote improvement of ecological conditions and introduction of cleaner hydrogen technologies.

Generalizing approximately 30 years experience of development of the HHM, we shall in detail observe on questions of HHP designing, as most complex heat machines with use of hydrides. The huge work which has been carried out all over the world on research and creation of HHP cannot be covered and generalized within the framework of one analytic review. In the submitted article questions of perfection of properties of metal hydrides will not be considered from the point of view of science of materials. Here attempt is made to present only some problems facing to developers of HHP with a tendency in area of thermodynamics and thermophysics of similar devices.

2. Bases of designing of effective HHPs

Procedure of creation of the heat machine based on periodic circulation of hydrogen and increase in the efficiency its operation demands the detailed information on methods of calculation equilibrium P - C - T (pressure - concentration - temperature) of characteristics, thermodynamic, thermalphysic (factors of specific heat conductivity λ and heat transfers α depending on temperature and pressure) and kinetic properties of hydrides. Approach to designing HHP as to an individual kind of HHM can be broken on three part [1]:

- Designing hydrides (definition of dependences of P - C - T , thermodynamic and kinetic properties);
- Designing reactor sorbers (increase and optimization of heat conductivity, maintenance of gas permeability, the coordination of processes of a heat transfer between heat carrier environments, the coordination of directions of heat and weights flows and so forth);

- Designing heat system (double, triple, multibank HHP) - the analysis of dynamics of operation of the heat pump, optimization of a cycle and other regime parameters.

In heat installations with use of hydrides efficiency of their operation (efficiency, quantity of heat (or colds) and heat capacity) depends on amount of the hydrogen participating in reaction. The amount reserved an alloy of hydrogen is characterized by equilibrium $R-S-T$ dependence which today define empirically. Let's open the specified directions in more details.

3. Choice of effective hydrides

General requirements to hydrides and approaches to their designing for HHP

To hydride heat devices the following requirements [2] are showed:

1. High sorption ability;
2. The big heat of formation of hydride;
3. High density for minimization of volume;
4. Easy hydrogenation;
5. The suitable characteristic pressure–concentration–temperature ($P-C-T$) in a range of temperatures from -20°C up to 200°C ;
6. High stability, explosion-proof - and a fire safety;
7. Low cost.

Requirements to hydrides determine their choice. The general number of hydrides known for today is rather great. Even the quantity of hydrides technically applied and satisfying the set forth above conditions is estimated in hundreds. Top T_h and bottom T_l levels of working temperatures of HHP define temperature borders in which the thermodynamic cycle can be made. Restriction bottom (for example, value of 0.05 MPa; at lower values of pressure of reaction of hydrogenation go languidly) and top (for example, no more than 5 MPa; at the big pressure it is necessary to solve questions of durability and increase in weight of a design of a sorber) pressure determine to us in coordinates pressure-temperature ($P-T$) borders in which should allocate $P-T$ of the characteristic of suitable hydrides. The additional task of average temperature level T_m on which should operation as HHP, basically defines temperature ranges for realization of an ideal cycle (Carno cycle) of HHP operation. Computer technologies at known set (and thus enough limited) properties of hydrides allow carrying out a preliminary choice of hydride pairs [3] at which the closed cycle is realized at the chosen operating conditions. The further analysis of chosen pairs can be carried out from the view point of obtaining of the best function ability, COP , adaptability to manufacture or profitability.

For a reliable choice of pairs hydrides, and also for designing hydrides it would be desirable to have universal $P-C-T$ dependence for hydrides. In the literature there is semi-empirical equation for equilibrium $P-C-T$ of dependences [4] where the data are generalized with use of function of free energy $RTL\ln(P/P_{xr})$ (where P_{xr} - scale of pressure for reference composition X_r , for example, taken in the middle a plateau of an isotherm of $P-C$). The given function reduces isotherms for various temperatures on one curve. Thus branches of isotherms of absorption and desorption can agree with a suitable choice of reference pressure P_{xr} . For

equilibrium structure the empirical formula for concentration of hydrogen in hydride [4] is received:

$$\left[\frac{H}{M} \right]_{eq} = \frac{a_1 a_2 X^{-a_3}}{(1 + a_2 X^{-a_3})} + \frac{a_4 a_5 X^{-a_6}}{(1 + a_5 X^{-a_6})}, \quad (1)$$

where $X = \exp[RT \ln(P/P_{X_r})] = (P/P_{X_r})^{RT}$, $a_1, a_2, a_3, a_4, a_5, a_6$ - empirical factors.

Function (1) appears enough good for reproduction of features of a characteristic curve in engineering calculations. With the help of this equation begins possible to project future intermetallic alloy by selection of necessary quantity of the alloying additive changing equilibrium pressure in hydride.

Ways of increase in efficiency of hydrides

In periodically working cyclic installations it is important to use hydride systems with the maximal contents of active hydrogen. Questions of revealing of new hydride materials are extremely important from the point of view of a ratio of the prices and efficiency. Concentration of active hydrogen depends on hysteresis $F_h = P_d/P_a$, a plateau slope $F_s = \ln(P_{C1}/P_{C2})/(C_1 - C_2)$. The hydrides most suitable to HHP under other approximately identical conditions are what have a small plateau slope and a hysteresis of pressure at absorption and desorption. This position is the basic from a point of view of increase in amount of the active hydrogen circulating in HHP, and improvements of HHP efficiency. For example, the amount of hydrogen in inverse proportion F_s also can decrease three times at change F_h with 0.9 up to 0.6. An ideal case is hydride which does not have hysteresis of pressure and plateau slope.

Duration of a cycle of HHP operation is defined as time required for reaction hydrogenation/dehydrogenation in pair hydride system. This time determines heat capacity of HHP. Duration of a cycle depends on kinetics of hydrogenation reactions, a heat transfer between the heated up and cooling environment, heat conductivities of hydride beds. Rates of reactions are proportional to a difference of dynamic pressure of hydrogen in sorbers of HHP and to constants of chemical reaction of hydrogenation. The relation of dynamic pressure is adjusted by characteristics of a heat emission in beds of metal hydride particles (the heat emission of a hydride bed depends on its effective specific heat conductivity) and connected to total factor of a heat transfer of system a sorber-heat exchanger. The modified constant of speed, as function of temperature in isobaric process [1], can characterize kinetics of sorption reactions. In HHP it is not sense to use hydrides with a low kinetics of reactions. The basic condition of an acceptability of hydride for HHP is a condition of forward rate of chemical reactions in relation to rate of a heat transmission.

4. Increase in an overall performance of hydride sorbers

To what it is necessary to aim at designing a hydride sorber

Process of a reversible sorption of hydrogen by intermetallides is chemical process. The certain speeds of chemical reactions which are defined by a kind of hydride and conditions of carrying out of reaction (pressure, temperature) is inherent in it. The sorption of hydrogen proceeds with allocation (absorption) and absorption

(desorption) of heat. Processes of mass (hydrogen) and heat transfer are characteristic for hydride beds. The knowledge of processes in hydride beds allows to increase their efficiency.

At realization of technical devices with use of hydrides by the basic original device, in which chemical reactions and processes transfer are carried out, the hydride sorber (reactor) is. Obligatory elements of a sorber are: the case, the hydride filler, the elements transmitting and filtering hydrogen, heat exchanging elements, stop and regulating armature. Hydride allocates beds (into which structure can enter and elements increasing heat conductivity) which are characterized by the geometrical sizes and effective characteristics (heat conductivity, a temperature conductivity, a heat capacity, gas permeability). Processes of absorption and allocation of hydrogen by hydride beds have non-stationary character. Duration and intensity of non-stationary processes heat and mass transfer in hydride beds we shall characterize dimensionless criteria: Fourier number - **Fo** and Biot number - **Bi**. Their connection with physical parameters $\mathbf{Fo} = a\tau/\delta_{ch}^2$, $\mathbf{Bi} = \alpha\delta_{ch}/\lambda_{eff}$ allows to formulate requirements to hydride beds. Here under δ_{ch} understand the resulted characteristic thickness of a hydride bed in a direction of action of a heat flow.

Characteristic time **Fo** defines dimensionless duration of non-stationary process and in inverse proportion to a square of characteristic thickness of bed δ_{ch} and in direct ratio an effective temperature conductivity a . For example, for increase of capacity of heat process in HHP it is necessary to reduce time of process. Active reduction of physical time of process will be promoted by reduction of thickness of bed δ_{ch} and increase in its temperature conductivity a .

The criterion of Biot **Bi** defines the relation between intensity of processes of external heat exchange (numerator of fraction) and effective heat conductivity of a hydride covering (denominator of fraction - complex $\delta_{ch}/\lambda_{eff}$). From the physical point of view this criterion characterizes uniformity of distribution of a temperature field on thickness of a hydride bed. In case of Biot criterion seeked to infinity, we have during the initial moment of time temperature on a heat exchanging surface equal to temperature of the heat-carrier (boundary conditions of the first kind) and the maximal non-uniformity of temperature on thickness of a bed. At **Bi** < 0.1 distribution of temperature on thickness of a bed can be counted approximately uniform and rate of reduction in average temperature of a bed coincides with rate of reduction in temperature of a heat exchanging surface. At designing hydride sorbers it is necessary to aim to small numbers of the Biot for the best carrying out of frontal chemical reactions of a sorption-desorption of hydrogen. To lower number **Bi** it is possible several ways: 1) reduction of the characteristic size of bed δ_{ch} ; 2) decrease in intensity of external heat emission α (but thus time of non-stationary processes will grow); 3) increase in effective heat conductivity of hydride covering λ_{eff} . To intensify processes of a heat emission in hydride beds at maintenance of uniform distribution of temperature in them it is possible by simultaneous increase in external heat emission α and increase in complex $\lambda_{eff}/\delta_{ch}$.

Other important characteristic of a porous hydride bed is its gas permeability - property of a porous material to pass through itself gas under action of the enclosed gradient of pressure. In conditions of viscosity mode of hydrogen flow in a porous bed the density of a stream of hydrogen is connected by linear dependence to a

gradient of pressure in the porous medium (Darcy's law). For the description of laminar flow of gases in pores sometimes use the equation of Gagen-Puazejlja which connects flow with properties of a porous body more obviously. Thus the real porous medium replace with the ideal medium consisting of system of round smooth channels of one diameter d_p . In this case connection of gas speed in the channel of porous body W_p and a gradient of pressure $\Delta P/l$ is described by the equation

$$W_p = \varepsilon d_p^2 (P_{in} - P_{out}) / (32 \mu a_{sin} l), \quad (2)$$

where ε - porosity of medium; d_p - diameter of pores, basically, unequivocally connected to the sizes of particles of hydride; $\Delta P = (P_{in} - P_{out})$ - the difference of pressure realized at length of a porous bed l ; a_{sin} - factor of pore tortuosity (relation of average pore length to thickness of porous bed δ_{ch}); μ - factor of viscosity of hydrogen.

Analyzing this equation with reference to hydrogen flow in hydride beds, it is possible to note a number of constructive measures which promote reduction of resistance of hydrogen flow ($P_{in} - P_{out}$): reduction of thickness of a bed of hydride (characteristic size δ_{ch}), passing hydrogen; reduction of pores tortuosity (a_{sin}) and increase in their diameter (d_p); increase in porosity of covering ε . Presentation of these requirements speaks about necessity of use for porous beds of structures with the open, organized porosity of small relative size ($l/d_p < 100$, at $\delta_{ch} = 5$ mm $d_p < 50$ microns).

At operation of HHP because of destruction of initial particles of hydride at a cyclic sorption the size of hydride particles in HHP decreases, that conducts to reduction of diameter of pores and increase in their tortuosity, and as consequence of it, to increase of hydraulic resistance of a hydride bed. Also at a sorption of hydrogen there is a process of compaction of a hydride bed because of increase in volumes of hydride particles that also results in increase in resistance of a bed. At a desorption is observed inverse process. For example, for a refrigerating cycle the incipient gradient of pressure (so-called "difficulty" of a filtration, i.e. a difference of pressure of hydrogen at the front hydrogenations and in a gas main) is most significant at a working part of a cycle, i.e. at cold production. It is connected by that pressure in a compressor part of a cycle (a preparatory half-cycle) approximately on the order is higher (depends on a concrete cycle), than at a working half-cycle (production of a cold), and intensity of heat and filtration processes thus is approximately equal. The aspiration to level duration of half-cycles demands approximate equality in them of mass flows of hydrogen. However, achievement identical with a preparatory half-cycle of the mass velocity ($W_{p\rho}$) in a refrigerating half-cycle because of lower pressure, and, hence, and density of hydrogen, is required approximately on the order the greater gradient of pressure. This circumstance is necessary for taking into consideration at designing a cycle of HHP refrigerator.

Thus, the filtration of hydrogen influences strong influence on dynamics of processes in a hydride bed, and calculation of transfer processes without taking into account a filtration can lead to incorrect results.

Let's stop on kinetics of chemical reactions. On uniformity of a warming-up of metal hydride layers depends both amount absorbed hydrogen and speed of a sorption. Numerous researches have shown that for rather high temperatures ($\tau > 250$

K) the kinetics of chemical reactions, at least, on the order exceeds heat diffusion in hydrides. Therefore for increase of the relation heat the capacity/weight is necessary to increase λ_{eff} and a .

Increase in effective heat conductivity of hydride beds

Generally heat conductivity of metal hydride powders complex depends on heat conductivity of an initial alloy, porosity of covering ε (ε - relation of free volume in a covering to all volume of an elementary cell), pressure of hydrogen in system and degrees of hydrogenation of a powder. At saturation by hydrogen heat conductivity of hydride decreases, since, as a rule, heat conductivity of an initial alloy many times over exceeds heat conductivity of hydride ($\lambda_m \gg \lambda_h$). Besides at transition in the sated condition heat conductivity of hydride becomes comparable to heat conductivity of gaseous hydrogen and by consideration of a composition hydride - hydrogen pressure of the last starts to influence heat conductivity of a hydride covering strongly. Effective heat conductivity of a hydride covering can be estimated, for example, under the formula:

$$\lambda_{\text{eff}} = \lambda_{\text{H}_2} \{5.8(1-\varepsilon) [(\ln(\lambda_h/\lambda_{\text{H}_2})/K) - 1 - K/2]/K + 1\}, \text{ at } \varepsilon > 0.3, \quad (3)$$

where λ_{H_2} - heat conductivity of hydrogen, $K = 1 - \lambda_{\text{H}_2}/\lambda_h$.

At absorption of hydrogen because of increase in volume of a hydride powder there is a reduction of porosity and improvement of contact of separate particles. It is a positive effect and finally results in increase in heat conductivity at tens %. At a dehydrogenating in a powder inverse processes, but here the contribution to heat conductivity from transition a hydride-alloy exceeds a relative loss from increase in porosity and easing of contact pressure.

Heat conductivity of hydride powders is insignificant, $\sim 0.3\text{--}1\text{ W/(m}\cdot\text{K)}$. For improvement of effective heat conductivity of a hydride reactor stuffing in it enter a skeleton from a high-temperature material (copper, aluminium, nickel). The design of such skeleton can be variously. For example, it can be as radial disks (a plate reactor), as a goffered insert (from the punched foil or a grid), the grids braided in a spiral, cellular bodies.

Heat conductivity of plate reactors, reactors with a goffered insert estimate on structural two-dimensional model depending on a direction of a heat flow under formulas [5]:

$$\lambda_{\text{eff}r} = (a/M)(a/L)\lambda_m + \{[(M-a)/L + (a/L)(\lambda_h/\lambda_m)^{-1}(1-a/L)]\lambda_h/[(M-a)/L + (a/L)(\lambda_h/\lambda_m)^{-1}]\} \dots \quad (4)$$

for a radial arrangement of elements of a skeleton and

$$\lambda_{\text{eff}a} = \{[1 - (1 - a/M)^2(a/L)(1 - \lambda_h/\lambda_m)]\lambda_h/[1 - (a/L)(1 - \lambda_h/\lambda_m)]\} \quad (5)$$

for an axial arrangement of repeating elements of a skeleton. Here a , M , L - resulted sizes (a - side of a skeleton of square section, M - side of an elementary cell, L - step of elements), λ_m - factor of heat conductivity of skeleton material.

Formulas are made with reference to the punched elements and for continuous elements considerably become simpler:

$$\lambda_{\text{eff}r}/\lambda_h = \lambda_m/\lambda_h(1 - \varepsilon) + \varepsilon \quad (6)$$

in a radial direction for continuous plates,

$$\lambda_{\text{eff}a}/\lambda_h = 1/[\lambda_h/\lambda_m(1 - \varepsilon) + \varepsilon], \quad (7)$$

in an axial direction, where ε - the porosity determined under the relation of volume without plates to full volume.

In case of application of high heat-conducting materials ($\lambda_m \gg \lambda_h$) takes place: $\lambda_{eff} \approx \lambda_m(1-\varepsilon)$, $\lambda_{eff} \approx \lambda_h/\varepsilon$. That is application of the radial copper ribs established, for example, with porosity $\varepsilon=0.9$ results in increase in effective heat conductivity in a radial direction (conterminous with a direction of a heat flow) up to values ~ 40 W/(m·K) and during too time heat conductivity in an axial direction remains small ($\lambda_{eff} \approx 1.1\lambda_h$). This restriction and also not adaptability to manufacture of a design result in limited use of plate reactors.

Application of foamy materials provides uniform on directions effective heat conductivity which can be estimated for the idealized three-dimensional structure under the formula:

$$\lambda_{eff3} = b^{-2} \{ \lambda_m + \lambda_h (b-1) [(b-1 + (\lambda_m/\lambda_h)(b^2+1)) / (1 + (\lambda_m/\lambda_h)(b-1))] \}, \quad (8)$$

where $b=L/a$, and the size b is connected to porosity the equation:

$$\varepsilon = 2b^{-3} - 3b^{-2} + 1. \quad (9)$$

The analysis shows, that for these structures λ_{eff3} there is only a function of a material of a skeleton and its porosity and weakly depends on heat conductivity of hydride. At characteristic for designs of reactors of porosity of cellular bodies (nickel, aluminium, copper) $0.9 < \varepsilon < 0.96$ effective heat conductivity changes over a wide range $3 < \lambda_{eff3} < 20$ W/(m·K).

To increase thermalphysic, technical characteristics on hydride materials it is possible, adding to them powders of high heat-conducting metals (aluminium, copper) and forming of them pressing compacts [6]. Methods of electronic microscopy confirm that at sintering such compacts in the environment of high pressure hydrogen the added metals form the porous matrix similar to cellular body's [6]. Effective heat conductivity of similar materials is estimated by empirical formulas, for example, [6]:

$$\lambda_{eff} = (1 - \varepsilon) \{ \lambda_m V_m / (1 + B_2 V_h^2) + \lambda_h V_h / (1 + B_1 V_m^2) \}, \quad (10)$$

where V_m and V_h - volume fractions of metal and hydride such, that $V_m + V_h = 1$; B_1 , B_2 - empirical constants.

Heat conductivity strongly depends on a weight part of metal in a compact, for example, for compacts $\text{LaNi}_{5-x}\text{Al}_x\text{-Al}$, $\text{MmNi}_{5-y}\text{Al}_y\text{-Al}$ λ_{eff} changed in a range $6 < \lambda_{eff} < 22$ W/(m·K) at change of contents Al $10 < \text{Al} < 30$ weight %.

The porous matrix not only increases heat conductivity, but also reliably keeps in the formed pores a metal hydride powder. There is an optimum value of part Al (~ 15 -18 weight. %) at which in a compact there is no sharp reduction of its gas permeability and thus $\lambda_{eff} \leq 10$ W/(m·K).

Other perspective method of binding of fine-dyspersated hydride in a porous metal matrix is "incapsulation" of an alloy, i.e. chemical coating of a thin porous bed of copper on a surface of particles of an alloy and its further forming under pressure [7]. Coating of copper by thickness 1 micron on particles of alloy $\text{LaNi}_{4.7}\text{Al}_{0.3}$ in the size 20 microns (the relation copper/alloy $\sim$ of 25 % on weight) and the forming from such capsules of tablets with pressure of 2 t/sm² provides obtaining of density of 4200-4500 kg/m³ and heat conductivities of 3.5 W/(m·K) in vacuum.

The most perspective on the technology, meeting the requirements of high heat conductivity, are methods of formation of porous matrix metal hydrides addition of the metal filler, cellular bodies or a preliminary encapsulation of a powder of an initial alloy.

Increase and the coordination of an internal and external heat emission of a sorber

Except for a problem of increase of effective characteristics of hydride beds there is a problem of the coordination of intensity external (between the heat-carrier and a wall of a reactor) and internal (inside a reactor) heat exchanging problems.

Generally in a heat exchanger of HHP takes place the balance of heat expressed by the equations

$$Q = GC_p \Delta t = K_{ht} \Delta t_{\log} F, \quad (11)$$

where G - flow of the heat-carrier, C_p - heat capacity of the heat-carrier, K_{ht} - factor of a heat transfer, F - heat exchanging surface, $\Delta t = t_{\text{out}} - t_{\text{in}}$ - difference of temperatures of the heat-carrier between its output and input, $\Delta t_{\log}$ - mid-logarithmic temperature pressure.

The flow of liquid G and received difference of temperatures Δt are connected unequivocally and consequently at desire to receive big difference Δt it is necessary to reduce the flow. The ratio between them is determined by mission of developed installation. For example, if necessary removal of heat of the certain temperature the liquid flow cannot be more than certain value. For removal of waste heat and acceleration of preparatory processes the fluid flow can be increased, as thus the difference of temperatures is not the limiting factor.

The factor of heat transfer K_{ht} is function of all chain on which passes heat exchange, and at one-dimensional (the flat case) heat exchange between a fluid and the hydride bed, divided by a technological heat-conducting wall, takes place:

$$K_{ht} = (1/\alpha + \delta/\lambda + R + 1/\alpha_{\text{eff}})^{-1}, \quad (12)$$

where α_{eff} - factor of an effective heat emission of a hydride bed; δ , λ - thickness of a technological wall and factor of its heat conductivity, R - contact resistance on border a wall-hydride bed.

The factor of the resulted heat emission of a hydride bed generally is proportional to effective heat conductivity of a bed and inversely proportional to thickness of a bed. The analysis of these equation shows, that factor of a heat transfer less than smaller factor of a heat emission and consequently it is of no used to increase strongly one of them, thus, not changing another. Results of experiments show, that for brazed and diffusion welded connections of the sorber case and heat-conducting insert $R = (0.5-1.5) \cdot 10^{-5} \text{ (m}^2 \cdot \text{K)/W}$. At contact of an insert and the case on tight fit R increases in 10-100 times and influence of contact resistance becomes comparable with influence of the resulted heat emission of a hydride bed.

Joint consideration of all these equations and mission of installation also define strategy of designing of hydride beds and heat exchangers. The strict decision of the transfer equations is a key to correct designing HHP. It defines importance and necessity of mathematical modelling of HHP.

5. Ways of increase of efficiency of HHP

The analysis of heat efficiency of HHP

The HHP, as well as all heat machines, are characterized by efficiency. Efficiency for various types of heat machines (a refrigerator, the heat pump, a heat transformer) calculates under various formulas, but the kernel remains same: useful

heat capacity is normalized on spent capacity. For demonstration of how efficiency is connected to designing, we shall consider efficiency of a refrigerator mode

$$COP_r = K_1 [\Delta H_B \Delta C_B - (C_{ph})_B (1 + (\varphi_c)_B K_k (T_m - T_l))] / \{ \Delta H_A \Delta C_A + (C_{ph})_A (1 + (\varphi_c)_A (1 - \lambda) K_k (T_h - T_m)) \}, \quad (13)$$

where ΔH - an enthalpy of hydride formation; ΔC - maximum quantity of hydrogen participating in a cycle; C_{ph} , C_{pk} - heat capacities of hydride and a material of a design accordingly; $\varphi_c = C_{pk}/C_{ph}$; K_1 - ratio between weights of hydrides **A** (high-temperature) and **B** (low-temperature), providing transfer of a maximum quantity of hydrogen; T_h , T_m , T_l - accordingly temperatures of high, average and low temperature levels of HHP; λ - degree of regeneration of heat in a cycle.

From the physical maximum of efficiency determined by the relation of enthalpies of hydrides **B** and **A**, real efficiency differs additional items included in numerator and a denominator of fraction. These items define influence of a heat capacity of a design on HHP efficiency, considerably reducing it. It is connected to necessity of cyclic transit of preparatory stages for a cycle (preliminary heating and preliminary cooling) and with the losses caused by it. Efficiency strongly depends on size of two-sided deviations from average temperature ($T_m - T_l$) and ($T_h - T_m$), decreasing at their growth. For increase of efficiency it is necessary to aim: 1) maximum to increase amount of transferable hydrogen in reaction ΔC ; 2) to increase heat of formation of hydride and in particular low-temperature hydride **B** (for example, application of hydrides on the basis of vanadium); 3) maximum to lower a total heat capacity of design, i.e. to reduce factor K_k . To weaken influence of parasitic stages of cycles on an overall performance of HHP also it is possible by essential increase of amount of the hydrogen participating in cycle ΔC . The best parameters on ΔC , realized today, make 0.8-1.2 weight. %. For creation of competitive HHP this figure is necessary for doubling.

There is one more way of reduction of losses of heat in a cycle which opens the whole direction in creation of HHP and schemes of functioning of HHP. This way is regeneration of heat. The degree of regeneration of heat in cycle λ is a heat quantity under the relation to all spent heat quantity which was useful is used for preliminary heating other sorber of HHP. Duration of a stage of regeneration is insignificant in comparison with duration of a cycle (for example, 1 mines at a level of 15 mines), but efficiency of it is great, since thus the maximal initial temperature potential ($T_h - T_m$) is used. Usually - $\lambda = 0.25-0.4$. In the patent literature circuit decisions of heat installations from the HHP using partial regeneration of removed heat for increase of efficiency of a cycle are offered many. Even in a two-level cycle application of regeneration is expedient. But it is necessary to remember, that realization of HHP with regeneration becomes complicated because of occurrence of new elements (a heat exchanging contour between identical sorbers) and stages of a cycle.

Reduction of weight of constructional materials of a sorber

Using an ideal cycle and available levels of temperatures T_m , T_h and T_l , it is possible to estimate theoretical maximal differences of temperatures of heating and cooling of hydride from average temperature with reference to problems of a heat transformation and production of a cold:

$$\begin{aligned}\Delta T_h &= (T_m/T_l) \Delta T_l, \\ \Delta T_l &= (T_m/T_h) \Delta T_h.\end{aligned}\quad (14)$$

From formulas it is visible, that at obtaining of additional heat and condition $\Delta T_h = \Delta T_l$ it is necessary to have lower value ΔT_l , rather than, than at obtaining of a cold value ΔT_l . It is connected to value of an additional factor. Substituting in these formulas the initial data on temperature of hydrides, it is possible to find out the maximal possible temperature deviations in a cycle from average temperature and to estimate an opportunity of performance of a mission of HHP (obtaining of a heat/cold of the necessary potential).

For the analysis influence of design weight on *COP* we shall present (13) in the simplified kind, assuming, that the heat capacity of hydride and a material of a design of a sorber is approximately identical both weights low-temperature *A* and high-temperature *B* hydride are equal:

$$COP = \frac{\frac{\Delta x(1-K_T)\Delta H_A}{C_p} - (1+K_K)\Delta T_l}{\frac{\Delta x(1-K_T)\Delta H_B}{C_p} + (1+K_K)\Delta T_h}, \quad (13')$$

where $\Delta X = \Delta C/m_h$ - normalized on weight of hydride amount of hydrogen (weight %), K_T - the factor showing the relation of weight of the heat-conducting filler m_T to weight of hydride m_h (the weight of the filler is a part of weight of a design).

Considering only numerator of fraction, it is possible to discover, as the weight of a design influences probably achievable level of reduction in temperature ΔT_l in a refrigerating cycle. At the given deviation of temperature ΔT_l , equating zero numerator in (13') and neglecting weight of the heat-conducting filler in comparison with other design, we shall receive the upper restriction of weight of a design $-K_{lim} = \Delta X \Delta H_A / (C_p \Delta T_l) - 1$. At the given deviations of temperatures $\Delta T_l, \Delta T_h$, in assumption $\Delta H_A \approx \Delta H_B$, $K_T \approx 0$ and the set efficiency *COP* the weight of a design should not exceed value:

$$K_K \leq \frac{\Delta X \Delta H (1 - COP)}{C_p (COP \Delta T_h + \Delta T_l)}.$$

For increase *COP* is necessary for raising ΔX , ΔH_B and to reduce K_T , K_K , ΔT_l , ΔT_h as obtaining of a cold with the help of HHP at level $T_l = -20^\circ\text{C}$ results in the lowest overall performance of HHP ($COP = 0.1-0.2$).

Increase of alloy output and reduction of hydrogen sorption time

The important characteristic for HHM efficiency is *the alloy output*, i.e. the heat capacity related to weight of hydride alloy. The value achieved for today on the average for a cycle makes 40-100 W/kg. At shortening of a cycle this value grows, but up to achievement of competitive (in comparison with other heat machines of similar type) value in 1000 W/kg [8] are necessary for increasing cardinaly amount of active hydrogen, to increase effective heat conductivity of a hydride bed and to optimize operation of system a sorber-heat exchanger. Thus duration of a full cycle is estimated $\sim 2-4$ minutes.

Non-stationary transfer processes in a sorber have exponential character. Process has a fast first phase and a slow, "tail" second phase. Basically hydrogen is

transferred to the first phase, but because of extended in time of the second phase the output of an alloy essentially (in times) decreases.

Change of dimensionless temperature in the middle of a flat hydride bed under boundary temperature conditions of the third kind is proportionally to expression [9]:

$$\Theta = \frac{T(0, \tau) - T_0}{T_{liq} - T_0} = 1 - \sum_{n=1}^{\infty} A_n \exp(-\mu_n^2 Fo), \quad (15)$$

where $A_n = f(\mu_n, Bi)$ and μ_n - roots of characteristic transcendental equation $\mu_n \operatorname{ctg} \mu_n = Bi$, $T(0, \tau)$, T_{liq} , T_0 - temperature: a hydride bed, a liquid, initial.

At $Fo > 1$ in expression (15) essential there is an influence only the first root of the transcendental equation. Expression (15) essentially becomes simpler - $\Theta = 1 - A_1 \exp(-\mu_1^2 Fo)$ and becomes available to estimations. If characteristic thickness of hydride bed $\delta_{ch} = 5$ mm, $\lambda_{eff} = 5$ W/(m·K), $\alpha = 1000$ W/(m²·K), $a \approx 2 \cdot 10^{-6}$ m²/s, $\rightarrow$ number $Bi = 1$. Then from [9] we find $\mu_1 = 0.86$, $A_1 = 1.12$ and temperature θ reaches the of 95 % of size (i.e. process of hydrogen transfer in an alloy will be approximately finished on 95 %) at $Fo \approx 4.2$ ($\tau \approx 52$ sec). Thus, at the general duration of a half-cycle in a sorber 8-10 minutes the basic part of process of hydrogen transfer occurs approximately for 1/10 durations of process. For increase of value of alloy output "tail" parts of half-cycles can be cut without serious consequences off. Power characteristics of hydride installation at shortening of a cycle can be finished up to competitive, but thus there are actual the problems connected to a cycling of hydride (reduction of capacity on hydrogen, disproportionation an initial alloy).

Thus the amount of the active hydrogen circulating between hydride sorbers a little decreases. To influence active amount of hydrogen it is possible, changing pressure of hydrogen at a charging of sorbers. As it has been shown in [11], there is a flat extremum for average on time of capacities of heating q_h , cooling q_c and COP depending on a level of initial pressure above hydride.

The coordination of operation of high-temperature and low-temperature sorbers

Actually, the decisions concerning to one sorbers of HHP have above been considered. Functioning of HHP as a whole is possible only at application at least two sorbers which are connected among themselves by a hydrogen line. In a line additional elements which clear hydrogen can be established and operate its stream (stop or check valves). Stop elements can not be. Then process of an exchange by hydrogen passes at approximately equal pressure in various sorbers and the basic mechanism controlled a mass transfer is heat exchange between hydride beds and the heating up environment. Intensity of heat exchange in low-temperature and high-temperature sorbers should be coordinated so that the certain amount of hydrogen, allocated in one sorbers, without a delay it has been absorbed in the other sorber.

At designing sorbers it is necessary to aim to that moving of front of sorption reaction did not result in essential change of a way of flow of hydrogen in a hydride bed. The similar problem exists in radial hydride beds where streams of heat and hydrogen can be directed to the different sides. Especially it affects operation of a low-temperature sorber during generation of a cold when in the beginning of process it is necessary for heat to pass through all hydride bed for maintenance of hydrogen desorption, and at the end of process at displacement of

reaction front to a wall is at a loss the output of hydrogen since it is necessary for it to overcome resistance of all bed. Therefore in refrigerator HHP the refrigerating part of a cycle should be designed better from a point of view of increase in intensity of heat exchanging processes.

The variant of HHP without the valve is realized especially easily for a modular principle of construction of sorbers. At absence of the stop valve in a hydrogen main general extent of a cycle because of more languid the current processes increases. Presence of the two-sided stop valve allows to force auxiliary operations of a cycle (preliminary heating and preliminary cooling) thanks to of more intensive heat exchange. Besides at a cross-over of hydrogen (at opening the valve) reactions of hydrogenation go faster since the kinetics of chemical reaction is proportional to a difference of hydrogen pressure in system and equilibrium pressure of hydrogen above hydride at the given temperature. The basic part of reaction passes for much smaller time, rather than, than at a variant without the valve. Therefore installation of the valve is desirable for obtaining of the best characteristics on capacity of HHP. In case of multistage cycles presence of stop hydrogen armature is obligatory.

Use of mathematical modelling for increase in an overall performance of HHP

Mathematical modelling is the important stage at designing HHP. At a successful choice of model of processes in HHP and at approach of modelled boundary conditions real conditions developers have an effective tool for fast check of constructive decisions.

For modelling operation of HHP the mathematical model and a set of computer programs [10-12] have been developed. The system of the modelling equations includes the non-stationary equations of heat balance in hydride sorbers taking into account of heat effects at absorption/allocation of hydrogen. Conditions at heat exchange of sorbers with external heat-carriers were taken into account, their real geometry and design features (materials and the sizes of walls, filters, height heat-conducting inserts, etc.). During modelling experimental data on equilibrium isotherms in systems metal alloy-hydrogen were used. Control of pump operation could be carried out differently: 1) by the definition of times of half-cycles, 2) the task of pressure restriction, 3) the task of restriction of temperature (a difference of temperatures). Dot and one-dimensional non-stationary models have been realized. At the first stage of calculations there was an opportunity to choose suitable pairs for which it was possible to realize a thermodynamic cycle for the given temperature borders. Thus the model allowed taking into account a hysteresis and a plateau slope of P - C - T of dependences. At the second stage in calculations the time cyclogramme of HHP operation was determined: temperatures of constructive elements, the contents of hydrogen in sorbers, pressure of hydrogen, heat flows to external heat-carriers and the basic power parameters - duration of the cycle, developed heat capacity, efficiency.

On the basis of alternative calculations there was an opportunity operatively to investigate influence of the various parameters determining a design and functioning of the heat pump that is important on a design stage for search of the best from the point of view of efficiency of HHP operating mode.

The further perfection of calculated model can consist in the account of a filtration of hydrogen through a porous bed, final speed of heat transfer in sorbers, influences of a kinetics of absorption and allocation of hydrogen. The expediency of use of the model which are taking into account only processes of heat and hydrogen transfer, explains practical absence of the data on the kinetic constants describing processes of a sorption of hydrogen in hydrides.

Use of multistage cycles in HHP

Present is enough the big global experience of construction of multistage hydride heat pumps. Here there is no opportunity in detail to analyse all features inherent in such pumps. We shall draw attention only to some integrating reasoning.

For influence on a temperature range (its expansion or compression) and improvements of efficiency binary heat machines (on two hydrides) have been modified for operation in multistage modes (triple heat pumps). The choice of three of hydrides and an estimation of efficiency of thermodynamic cycles for such HHP can be determined, basing on the approaches developed in [13, 14].

That efficiency of HHP could be improved at use of the multistage modes, replacing hydrides (instead of one hydride) should have lower values of a heat capacity. Also it is necessary to remember, that the most systems suggested for triple heat pumps, more reduce, than expand areas, temperatures possible for double hydride systems. Thus hydraulic and gas hydrogen systems for installations with three hydrides considerably become complicated.

6. Conclusions

Thus, it is shown, what thermalphysic methods and in what limits it is possible to improve effective operation of hydride heat machines. The basic deterrents of wide application of HHP are restrictions which are imposed by hydride materials. In modern conditions for substantial improvement of characteristics of HHP it is necessary to raise capacity of hydride on hydrogen a minimum in 2 times (with 1.5 up to 3.0-3.5 weight. % for a range of working temperatures close to room).

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COMPUTER MODELING OF IONS H^+ , H_3O^+ , H_5O_2^+ TRANSPORT IN NANOSTRUCTURAL SUPERMOLECULES OF WATER

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Abstract. Features of energetic barriers for track transport of aquatic ions of hydrogen and go-ahead track carry of single proton in water within the framework of quantum-field chemistry theory and methods of computer modeling are investigated. On the basis of calculations it is proved that the energetic barrier (9 kJ/mol) of single proton track conduction through cellular nanostructure of water is in a good agreement with experimental data. It is situated essentially below similar barriers for track transport of aquatic ions H_3O^+ , H_5O_2^+ (130 kJ/mol and 111 kJ/mol, respectively). It is clarified how a single proton track conduction provides mechanism of effective ions H_3O^+ conductivity, which differs from well-known Grotthuss mechanism. The contribution of aquatic ions (H_3O^+ , H_5O_2^+) track conduction to carry of charges inside of the cellular nanostructure of the condensed state of water is very small. They are strong confined inside of cells bounded by water supermolecular walls $(\text{H}_2\text{O})_n$. Transport of these aquatic ions of hydrogen can occur only on the areas lying outside of supermolecules of water.

Keywords: nanostructure, aquatic ion of hydrogen, proton conduction, computational chemistry, modeling

1. Introduction

It is known [1] that transport of a proton in various condensed states of water plays a key role in hydrogen conversion of energy. There is much controversy over the mechanism of this proton motion [2-4]. Most explanations rely on the basic Grotthuss mechanism. According to this mechanism, a proton from an H_3O^+ ion moves rapidly along a hydrogen bond to neighboring water, so recreating the H_3O^+ on the neighboring molecule. Another proton from the receiving water molecule then translocates similarly to another neighbour, etc.

Recent progress in understanding proton conduction has been made using developments in *ab initio* computer simulations [2]. But it is important to note that calculated energetic barrier of proton carrying on Grotthuss mechanism is very small (~ 1 kJ/mol) [4], because it corresponds effectively to proton track moving across ideal molecular lattice of water. This theoretical estimation is in contravention of experimental magnitude of the energetic barrier of proton carrying in liquid water that is equal to 8 J/mol and can become very large (~ 80 kJ/mol), when a proton moves in specific water channels of biochemical systems [3].

The nature of large additional energetic barriers on path of proton jump from one molecule of water to another is not revealed. Up to now mechanisms of transport of aquatic ions H_3O^+ , H_5O_2^+ and go-ahead carry of a proton in the

condensed phases of water are insufficiently investigated. In the given work we try to develop more real approach to this problem on the basis of quantum-field chemistry concept [5-8].

2. Basic approaches

Proton transport in aqua solution is an electrochemical process that is important not only for numerous biochemical reactions, but it plays a fundamental role in the generation of power in fuel cells. It is connected by that a proton is the basic agent of go-ahead carry of a charge in the water solutions used in fuel cells, as it is shown on Fig. 1.

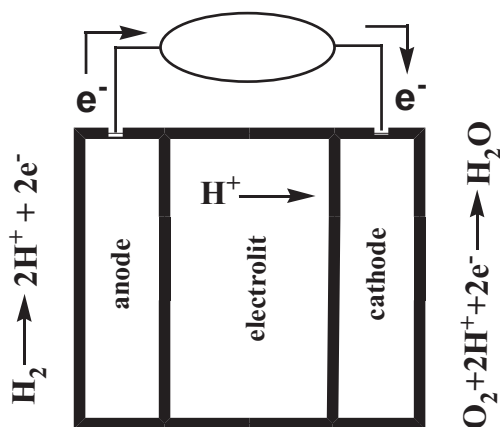


Figure 1. Scheme of go-ahead carry of a charge in the water solutions used in fuel cells

High mobility of the proton gives the unique go-ahead mechanism of "carry" of ions H_3O^+ and OH^- according to well-known basic Grotthuss mechanism [4]. At the same time, transport of cations and anions is complicated by their blockage in cellular nanostructures of the condensed phases of water. Real mechanisms of transport of aquatic ions H_3O^+ , $H_5O_2^+$ and go-ahead carry of the proton are to involve strong blockage interaction of charged conducting particles with intramolecular bonded grids of water supermolecules $(H_2O)_n$.

Quantum-field chemistry approach [5-7] treat structures of the condensed phases of water as a spatial system of multiparticles of water $(H_2O)_n$, which is modeled by scheme shown on Fig. 2.

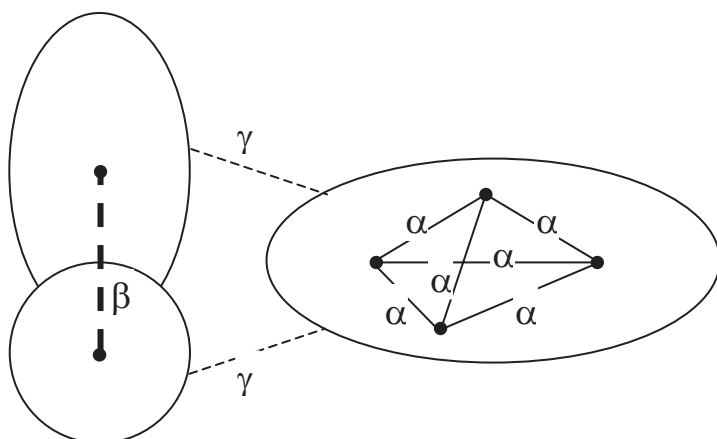


Figure 2. Structure of the condensed phases of water in quantum-field chemistry.

The internal structure of each such supermolecule includes some spatial grid of intramolecular hydrogen (O—H—O) α -bonds [6,7]. Supermolecular multiparticles interact with each other by using intermolecular bonds. There are two kinds of such bond: supramolecular exchange H-bond classified as adhesive chemical (O—H...O) β -bond and intermolecular no-exchange physical γ -bond [6-8]. Thus, transport of aquatic ions of hydrogen inside the condensed phases of water is carried out through emptiness of two kinds. First of all, it is intramolecular emptiness restricted by grid intramolecular hydrogen (O—H—O) α -bonds and, secondly, it is supramolecular emptiness confined by network of supramolecular hydrogen (O—H...O) β -bonds and blocking electrostatic γ -bonds.

3. Results and Discussion

In the given investigation we taking under consideration transport of aquatic ions of hydrogen and a proton on areas laying inside supermolecule $(\text{H}_2\text{O})_n$, which is shown on Fig. 2.

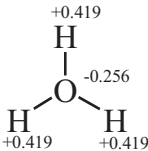
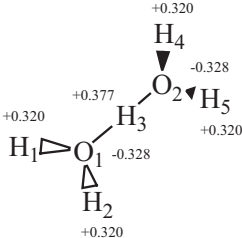
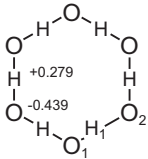
Their grids form a cellular nanostructure of multiparticles of water. It is well known that ring fragments (O_6H_6) form most penetrable walls of water cells. Six intramolecular hydrogen (O—H—O) α -bonds connect six atoms of oxygen in stable ring of opposite charges having about 0,6 nm across diameter. Transport of any ions through cellular grids of aquatic supermolecule has as the basic limiting stage overcoming the most penetrating barriers that lay in a direction of an axis of a ring wall (O_6H_6) of water cell.

Between the wall of the cell and any ions (H^+ , H_3O^+ , H_5O_2^+) forces of supermolecular hydrogen β -bonds and electrostatic γ -bonds operate (see Fig. 2). Surfaces of intermolecular potential energy have been calculated by density functional method stated in our paper [6]. Necessary data about spatial distributions of electron charge density inside framework of aqua multiparticle had been taken from calculations of aquatic ions and the ring of water $(\text{H}_2\text{O})_n$ by using of standard molecular orbital method in the minimal basis set (STO-3G). Results of calculations are shown in Table 1.

On Fig. 3 diagrams of the basic stages of aquatic cautions H_3O^+ and H_5O_2^+ passage through water ring and the basic intermolecular interactions for optimum

geometry are shown. Calculated potential curves of transport for aquatic ions H_3O^+ and H_5O_2^+ through a cyclic fragment are also shown on Figs. 4, 5. According to our calculations there is very high barrier (130 kJ/mol) in case of conduction of aquatic ion H_3O^+ through the cyclic fragment of supermolecular cell of water. The high barrier is connected with forces of pushing away of aquatic ion H_3O^+ from the ring at attempt to pass through it. When a proton in the form of symmetric aquatic ion H_5O_2^+ carrying through cyclic fragments of the aqua cell there are two peaks of barrier: a high external peak of barrier (~ 111 kJ/mol) and low internal peak of barrier (~ 67 kJ/mol). In this case the high peak of barrier is connected with forces of pushing away, and another with forces of an attraction of a proton to ions of oxygen in the cycle of aqua wall. The internal barrier exists only for proton carrying in the form of symmetric aquatic ion H_5O_2^+ .

TABLE 1. Calculated parameters of aquatic ions and supermolecular ring of water

Ion system	Parameter	Value
	$L(\text{O}-\text{H}), \text{\AA}$	0.99
	$\alpha(\text{H}-\text{O}-\text{H}), \text{degrees}$	113.8
	$L(\text{O}_1-\text{H}_1), \text{\AA}$	0.98
	$L(\text{O}_1-\text{H}_3), \text{\AA}$	1.16
	$\alpha(\text{H}_1-\text{O}_1-\text{H}_2), \text{degrees}$	107.5
	$\alpha(\text{H}_1-\text{O}_1-\text{H}_3), \text{degrees}$	116.5
	$\alpha(\text{O}_1-\text{H}_3-\text{O}_2), \text{degrees}$	178.7
	$L(\text{O}_1-\text{H}_1), \text{\AA}$	1.03
	$L(\text{O}_2-\text{H}_1), \text{\AA}$	1.80
	$\alpha(\text{H}-\text{O}_1-\text{H}_1), \text{degrees}$	117.9
	$\alpha(\text{O}_1-\text{H}_1-\text{O}_2), \text{degrees}$	177.8

On Fig. 6 it is shown a surfaces of potential energy barrier for passage of single proton through the ring (O_6H_6). Calculated magnitude of barrier height is about 9 kJ/mol that is in a good agreement with experimental data. In addition it is obvious that the barrier of single proton transport through supermolecule cell of water is essentially less than analogical transport barriers for its aquatic ions H_3O^+ ,

H_5O_2^+ . Therefore in offered model of quantum mechanisms of aquatic ion blockage in a specific cellular nanostructure of the condensed phases of water it is obvious that only one channel of track conductivity is real. This channel operates as a result of track moving of single protons through ring "windows" (O_6H_6) of cellular nanostructure of water.

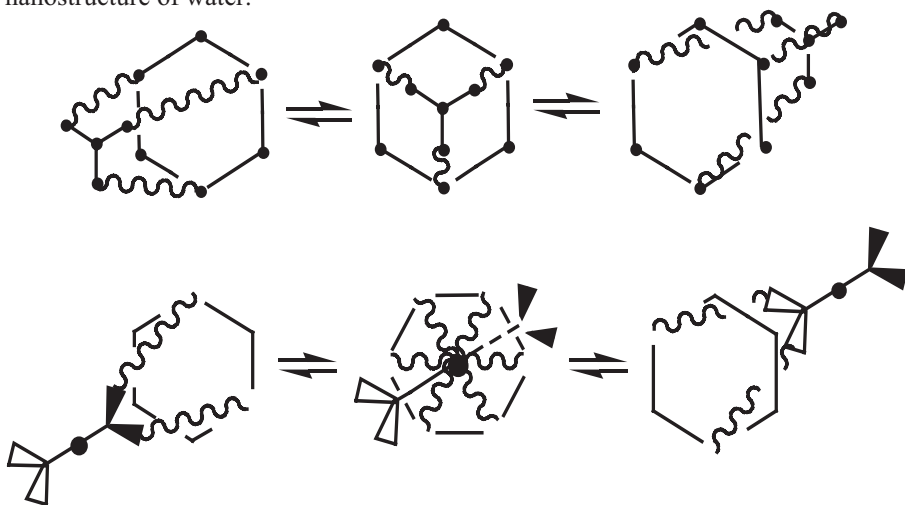


Figure 3. Model of transition H_3O^+ and H_5O_2^+ through the circle (O_6H_6).

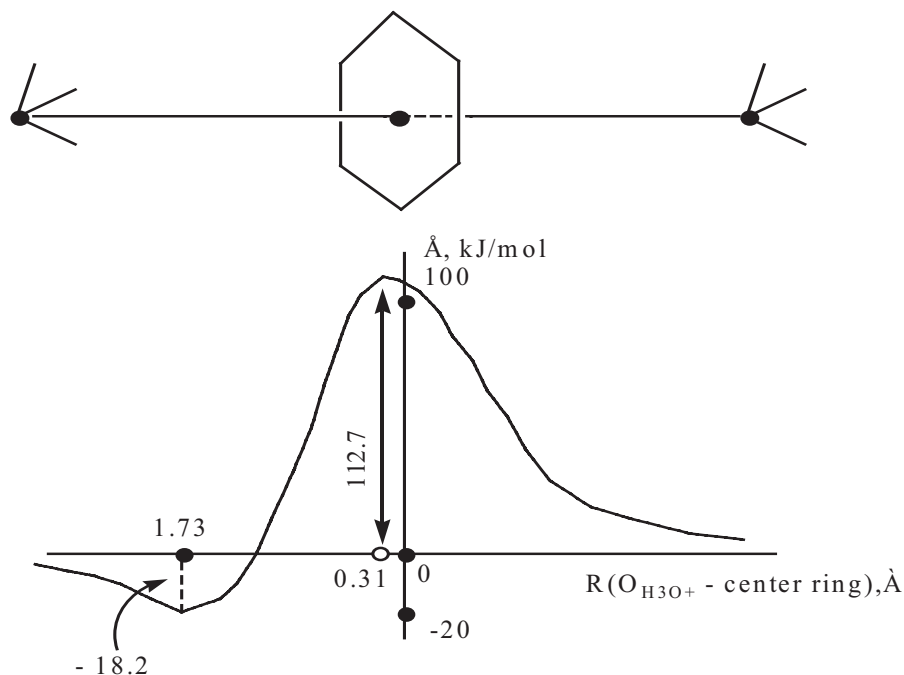


Figure 4. Potential curve of passage of ion H_3O^+ through a cyclic fragment (O_6H_6).

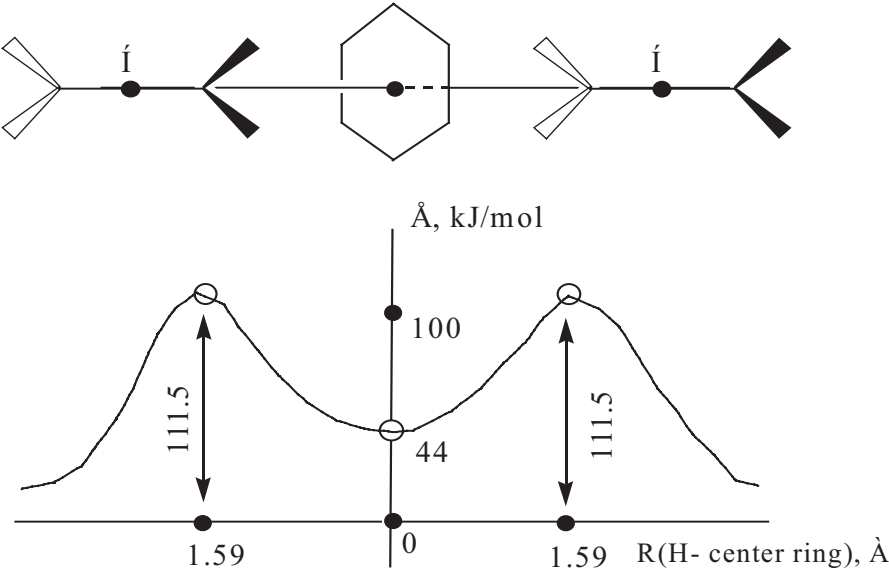


Figure 5. Potential curve of passage of ion H_5O_2^+ through a cyclic fragment (O_6H_6) .

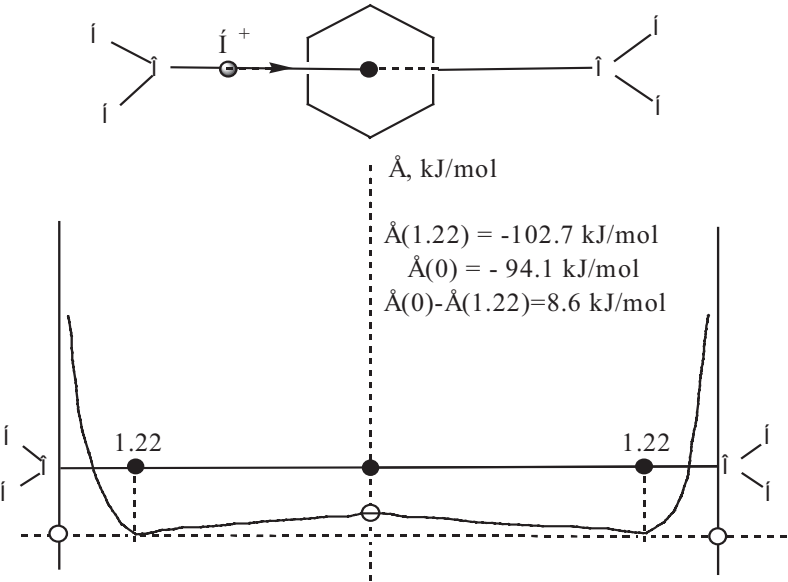


Figure 6. Potential curve of passage H^+ through a cyclic fragment (O_6H_6) .

4. Conclusions

In conclusion we wish to give some common remarks in regard to current affairs in the field of theoretical explanation of proton conductivity in water solution.

Some researchers [3] noticed that high magnitude of the power barrier of proton transport in specific water channels is caused from existence of strong electrostatic blockage in real environmental conditions. This point of view has been originally accepted by biochemists.

Recently other investigators [2] tried to give an explanation of apparently high magnitude of the power barrier of proton at transition in a real liquid condition suggest that there is an infringement of mesh structure of aqua solution when proton moves rapidly along a hydrogen bond between neighboring molecules of water. They found that proton conduction depends critically on whether the environment is acidic or basic. The illumination of different mobility mechanisms operational in acidic and basic environments may help to clarify why nature might prefer acidic or basic conditions in different situations involving proton transport, and ultimately to exploit the different mechanisms in the design of processes or materials that utilize proton conduction phenomena. The researchers demonstrated that, in fact, no such simple chemical analogy exists between H_3O^+ and OH^- . For example, showed that OH^- is surrounded, on average, by 4-5 water molecules, quite unlike the hydronium case. Moreover, proton conduction in bases requires more complicated rearrangements of water molecules than in acids. Finally, the process is strongly influenced by a phenomenon known as quantum tunneling, a phenomenon that can occur at the microscopic level, which allows particles to traverse spatial regions they normally should not, provided they do it quickly enough. They suggested that it results in changes of the nature of the mechanism of proton carrying in aqua solution.

Note that our explanation of strong dependence of magnitude of potential energy barrier for proton conductivity in water solution on specific nanostructural conditions is, at bottom of fact, complementary to the well-known thesis offered by abovementioned investigators.

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INDUSTRIAL TECHNOLOGIES FOR PRODUCTION OF LaNi_5 -BASED HYDRIDE MATERIALS

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Abstract. In present work we bring to your notice the main characteristics of the industrial technologies concerning production of LaNi_5 -based hydride materials (HM) by means of metal component melting and by CaH_2 treatment of oxide and metal mixtures. Here one could also get an idea about the influence of these technologies on the structure and properties of the received materials.

When producing ingots the La range in chemical composition was 30,34-33,79 (%wt) which corresponds to the formula $\text{LaNi}_{5,43}$ - $\text{LaNi}_{4,64}$. But due to homogenous areas of LaNi_5 under temperatures higher than 1000°C and also due to rapid crystallising (tempering) while cooling down in a metal casting form with intensive heat removing there was identified a single-phase state of material (100% LaNi_5).

Trying to get the material by means of CaH_2 treatment of oxide and metal mixtures we can say that long-term isothermic exposures and slow cooling process, in case of any deviation of chemical composition from stoichiometric one (La 32,13 %wt), will result in appearances of second phases (La_2Ni_7 or Ni) worsening the alloy properties. Following this method we could ensure producing of alloys with an appropriate structure and satisfactory level of service characteristics by means of charge calculations with a slight Ni excess (2 max %, wt) if compared with stoichiometric composition.

Keywords: alloy, melting, reduction, intermetallide, hydride, hydrogen.

1. Introduction

Nowadays a number of trends in the hydrogen energy industry involved in researching hydride materials (HM) are on the brink of introducing such materials into industry. As a result there obviously arises a vital need in technologies for industrial production of the said materials.

There is sensitive La in the alloys based on intermetallic compound LaNi_5 . If discussing production of large quantities of the said materials by metal component

melting we could single out the following types of melting: induction, arc with consumable and non-consumable electrodes and electron-beam (EB).

Alloys requiring high accuracy of composition are usually melted in vacuum induction furnaces allowing a good mix of all components but there's a danger of introducing alloys with non-metallic admixtures due to interaction of a sensitive component with the material of a ceramic crucible. The shortcomings of this melting type also refer to the fact that the cost of melting in an induction vacuum furnace is considerably higher than that in an arc vacuum furnace and output is lower.

Arc melting in the furnace with non-consumable electrode is applied mainly under lab conditions for quick producing of small melt samples. The main characteristics of this melting type are low accuracy of composition control due to complicated mixing of components and also increased alloy impurity with the electrode material (carbon/tungsten). That's why arc furnaces with non-consumable electrode are seldom applied for alloy melting under industrial conditions. They're usually used to melt ingots out of sponge or powder-like materials employed further as consumable electrodes [1]. As metallic La isn't produced due to its high sensitivity when in the form of sponge or powder, we can't consider this way of receiving LaNi_5 either. Metallic La is produced in the form of compact ingots of rectangular shape. As it's difficult to get electrodes using these ingots we excluded such melting types which demand usage of consumable electrodes – arc and EB meltings. So to get LaNi_5 by means of metal component melting we applied induction melting with vacuum and rare gas.

For production of alloy powders containing rare-earth and other active metals we consider the method of CaH_2 treatment of oxide and metal mixtures (CaH_2 method) as the most preferable concerning correlation of cost and quality [2-4]. Here we use certain oxides as raw material containing sensitive metals which is considerably cheaper than metal components.

Currently we're mastering both industrial technologies of LaNi_5 production by CaH_2 and melting methods. We've also produced and tested large lots of materials.

2. Experimental details

The technology of LaNi_5 production by means of metal component melting was developed at Baikov Institute of Metallurgy and Material Sciences together with Moscow Experimental Plant of Quality Alloys. They used induction melting in an OKB-869-type furnace (capacity 150kg, power 100kvt) for LaNi_5 production.

Purity of the starting materials was 99,8%. Nickel was loaded right into a magnesite crucible. To prevent La burning out it was loaded into special cavities inside the furnace. Ni was melted in vacuum with the residual pressure of appr. 4×10^{-7} MPa. Ni melting down completed, the furnace was introduced with argon (0,04-0,06 MPa) and then with La in several doses. Later alloy was poured into a preliminary heated up to 200-300 C casting form followed by ingot cooling down till 200 C right in the furnace (further cooling of the casting form was conducted in the air media). The received material was crumbled into powder in a special vibroabrading device. Taking into consideration pyrophorosity of the composition

they worked out optimal grinding procedures allowing to get powders sized 100 μm max.

CaH_2 technology for LaNi_5 production was developed at JSC “Polad”, Tula. They used (electrolytic) Ni powder with purity of 98,6%, La oxide (purity 99,93%) and CaH_2 (CaH_2 content 99% min). Powders of Ni, La oxide and CaH_2 were mixed, then loaded into a steel container and heated under 1000-1200°C for 10 hours till full reduction as per reaction:



Reaction product is a solid substance consisting of baked particles of LaNi_5 and CaO . To separate alloy from CaO semi-finished product was crushed and water treated per reaction $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$. To transfer Ca(OH)_2 into a soluble compound the received substance was treated with hydrochloric acid per reaction: $\text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$, then CaCl_2 was washed out with water. This done, the received powder of LaNi_5 was dried and sieved.

They used X-ray fluorescent method to do chemical analysis of the received materials and diffractometer DRON-3M for roentgen-phase analysis ($\text{K}\alpha$ -Cu radiation with graphite monochromator). For comparison they referred to data of PDF (Powder Diffraction File) Bank. Sorbtion characteristics (pressure of hydride formation and sorbtion capacity) were defined by means of P-C isotherms drawing while received materials interact with hydrogen in the apparatus of Cubeptca type (Sieverts – type apparatus).

3. Results and Discussion

3.1 METHOD OF METAL COMPONENT MELTING

This technology was involved in producing of more than 3 tons of alloys meeting the compound of LaNi_5 . Samples for chemical analysis were taken from top, middle and bottom parts of the ingot with the following dimensions (mm): length – 200, width – 70, height – 450. The analysis results are given in Table 1.

In the course of the experiment we found that in 4 ingots the range of La chemical composition was 30,34 - 33,79 (%wt) which corresponds to the formula $\text{LaNi}_{5,43}$ – $\text{LaNi}_{4,64}$. It results in the range of pressure value for hydride phase dissociation, formed when hydrogenating materials of such compositions, of appr. 0,2 – 0,8 MPa [5]. The given range of chemical composition including the one within a single ingot could be referred to liquating processes when crystallising. Radiographic shooting with Theta angles of 2,5-40 degrees revealed 69 lines. In table 2 you can find data (Two Theta, d – cleavage spacing, I –intensity) for the most intensive of them. For you to compare we also give there data of PDF Bank for LaNi_5 (map 17-126). In table 2 you could easily find full coincidence of reflexes in Theta angles but the intensity of the lines differs which betrays a strongly grain-oriented structure due to material reducing into powder. Analysing the results we found a 100% phase of LaNi_5 in the material structure.

TABLE 1. Chemical analysis of LaNi₅ in an industrial lot of alloy

No. ingots	Sample place in the ingot	La content (%wt)
1	top	31,14
	middle	32,19
	bottom	32,43
2	top	31,72
	middle	31,95
	bottom	31,61
3	top	31,58
	middle	30,34
	bottom	31,50
4	top	31,55
	middle	33,79
	bottom	31,74

TABLE 2. Data of X-ray diffraction for LaNi₅

Measured sample			PDF Bank, map 17-126	
Two thete, degree	d, Å	I, rel. unit	d, Å	I, rel. unit
35,89	2,502	49	2,500	30
41,65	2,168	61	2,169	32
42,60	2,122	12	2,119	50
47,83	1,902	100	1,905	20
59,26	1,559	33	1,558	15
61,06	1,518	22	1,515	10
75,73	1,256	11	1,255	40

Homogenuous state in the structure was achieved due to the area of homogeneity for LaNi₅ under temperature of 1000°C min [6] and due to rapid crystallising (tempering) when cooling down in a metal casting form with intensive heat removing.

3.2. CAH₂ METHOD

Charge treatment under high temperatures is done owing to external heating in shaft furnaces. The accompanying processes are rather complicated as per reaction (1) but we can single out the main of them. The first is reaction of La oxide reduction, the other is interaction of La under formation with Ni leading to production of LaNi₅.

Under temperatures higher than 800°C CaH₂ is decomposed into Ca and molecular H and the reducing agent here is virtually metal Ca in liquid and partly gas states [2]. So we can depict the reaction of La oxide reduction as:



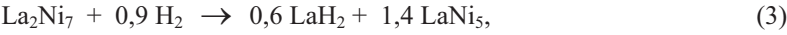
Thermodynamical analysis showed a high probability of this reaction passing under temperature higher than 800°C, e.g. change of Gibbs energy $\Delta\dot{G}^\circ$ for reaction (2) under 1000°C is 24,4 kcal/mole, under 1200°C $\Delta\dot{G}^\circ = -23,12$ kcal/mole. Moreover the reaction direction is decentered to the right owing to interaction b/w La and Ni resulting in formation of LaNi₅.

Specific heat effect of reaction (1) playing an important role in CaH₂ reduction is 96 kilocalorie per 1 kg of charge but its rate is far from dangerous if taking into consideration safety measures [2].

In general reduction reaction passes smoothly and no technological difficulties were found. The main stress is to be put on the process of formation of intermetallic compound LaNi₅.

Developing this technology we had in mind the necessity to get homogenous alloy powders in the system of Ni-La with the phase composition corresponding to LaNi₅ close to 100 %. As per diagram of Ni-La state [6] the peculiarity of this composition is the absence of homogeneity area under temperature lower than 1000°C. It does cause certain difficulties in the technology as any deviation in La content in the alloy from stoichiometric one (32,13 %,wt) leads to appearance of other phases worsening alloy properties. Long-term isothermic exposure and slow cooling process characteristic of CaH₂ reduction allow to define this process as thermodynamically equilibrium. That's why phase composition of alloys should meet equilibrium diagrams of state for corresponding systems. In this case under process temperature of 1000 - 1200°C La formed out of oxide per reaction (2) interacts with Ni forming then liquid melt which in its turn when hardened forms crystals of LaNi₅ or LaNi₅ or La₂Ni₇ depending on the initial charge composition. If Ni in the charge is in excess but for LaNi₅ there should be present Ni particles which remained insoluble.

Table 3 gives an idea about calculated phase content in the alloy Ni-La depending on La content close to LaNi₅ compound. We advise to avoid La₂Ni₇ phase in the alloy as its sorption characteristics are much worse than those of LaNi₅. Besides we know that intermetallide La₂Ni₇ is subject to hydrogenolysis when interacting with hydrogen, that is to decomposition into LaH₂ and Ni or composition enriched with Ni, e.g. per reaction:



and it's not used as hydrogen sorbent [7].

TABLE 3. Calculated phase content in Ni-La alloy

№	Calculated La content in charge (%,wt)	Calculated phase content (%)		
		LaNi ₅	La ₂ Ni ₇	Ni
1	32,13	100		
2	33,13	87,8	12,2	
3	34,13	75,6	24,4	
4	31,13	97		3
5	30,13	94		6
6	40,34		100	

Liquid phase of La₂ Ni₇ is formed in the course of initial charge treatment under temperature of 995°C min as its melting point is 995°C while that for LaNi₅ is 1350°C which often results in half-melting of reaction products and problems with furnace equipment. Due to the presence of La₂ Ni₇ phase in powder alloy with high content of La (40, 34 %,wt) its oxidation increases at air contact. From the other side appearance of Ni phase doesn't influence characteristics of the received alloy so greatly nor worsens processibility of alloy production but lessens alloy sorbtion capacity as an outside phase [8].

In table 4 you can see characteristics of LaNi₅ powders reduced from charge with La content 32,13 (%,wt) that is in conformity with its mass fraction in chemical formula. Powders were chemically and X-ray diffractionally analysed; sorbtion characteristics were defined in State Institute of Nitrogen Industry in Moscow. Before analysis sorbents were activated by a 3-time hydrogen introduction onto a vacuum-treated hot sample with the subsequent cooling till room temperature in hydrogen media. Heating temperature was 150°C max, pressure – 7 MPa max.

Data in table 4 permit us conclude that there's no stability in production of homogenous powders in each lot. In the majority of cases we found other phases of La₂Ni₇ or Ni present. And the best sorbtion characteristics belong to powders with a 100% content of LaNi₅ phase or with a small Ni content. Should powders have hydrogen capacity of 140 cm³/g min they can't be used for this compound.

Analysing reasons for such situation we can say that it's rather difficult to get calculated content of La. Many factors of the process of charge treatment with CaH₂ lead to the fact that it's impossible to avoid deviations of La content in the product, especially under industrial conditions, in both directions, e.g. owing to

irregular mixing of charge components or insufficient accuracy of their measuring, irregular heating while reducing – diffusion, etc.

Taking into consideration that La content increase for 1% compared with stoichiometric one results in the appearance of 12,2% La_2Ni_7 phase with all the other consequences and content decrease even for 2% gives only 6% of pure Ni (see tab.3), we suggest charge be calculated per La content a bit lower than in the formula of intermetallic compound.

TABLE 4. Properties of LaNi_5 powders from experimental lots

Lot No.	Chemical composition (%wt)				Phase composition (%)			H capacity (cm^3/g)
	Ni	La	Ca	O ₂	LaNi_5	La_2Ni_7	Ni	
1	base	30,8	0,460,8		95	5		150
2	-31,95	0,370,5			100			165
3 *	-33,0	0,8	1,8		85	15		120
4	-31,53	0,3	0,4		100			170
5	-32,88	0,9	1,6		90	10		125
6	-32,3	0,650,9			95	5		140
7	-31,04	0,41	0,58		97	3		158
8	-32,84	0,68	1,24		90	10		130
9 *	-33,45	0,752,0			78	22		< 120

TABLE 5. Properties of LaNi_5 -based alloys

№	Alloy formula	H capacity, cm^3/g	Pressure of H dissoassiation, MPa	
			20 °C	100 °C
1	Ni_5La	170	0,14	1,8
2	$\text{Ni}_{4,8}\text{Al}_{0,2}\text{La}$	151	0,054	0,9
3	$\text{Ni}_{4,8}\text{Al}_{0,2}\text{La}_{0,9}\text{Ce}_{0,1}$	146	0,063	1,1
4	$\text{Ni}_{4,98}\text{Al}_{0,02}\text{La}_{0,5}\text{Ce}_{0,5}$	170	1,0	9,8
5	$\text{Ni}_4\text{CoLa}_{0,5}\text{Ce}_{0,5}$	165	0,8	-
6	$\text{Ni}_{4,98}\text{Al}_{0,02}\text{La}_{0,95}\text{Ce}_{0,05}$	160	0,21	2,5
7	$\text{Ni}_{4,95}\text{Al}_{0,05}\text{La}$	156	0,1	1,6

Note: alloy powders have a single phase and correspond to the phase of LaNi_5 type

In Table 5 you'll find properties of some alloys on LaNi_5 -basis produced under industrial conditions designed for each alloy depending on its physical and chemical properties: charge composition, temperature of its treatment and time of isothermic exposure, procedures of hydrometallurgical treatment of reaction products.

Dispersion of alloy powders is within the range of 3-160 μm with 80-90% of particles sized 40-100 μm ; bulk density of powders is 3,45 – 3,55 g/cm^3 ; flowability 30 – 40 sec; particle shape is mainly fragmental. Powders are badly formed, particles are brittle and easily crushed.

Powders are unstable in acid media and stable in alkalai ones, they are actively oxidated when heated in air or water media. Shelf life in the air media under standard conditions is about several years.

4. Conclusions

We present main characteristics of two industrial technologies for production of hydride materials on the basis of intermetallic compound LaNi_5 .

We show that the technology based on the method of metal component melting with rapid cooling down of ingots in a metal casting form shall result in production of a single-phase alloy with chemical heterogeneity ($\text{LaNi}_{5,43}$ - $\text{LaNi}_{4,64}$) within a high-temperature range of LaNi_5 homogeneity.

We've developed a new technology of LaNi_5 -type material production by means of CaH_2 treatment of oxide and metal mixtures (CaH_2 method). The material reduced following this technology is powder with main particle size up to 160 μm . Hydrogen sorbtion capacity for this material is 150-170 cm^3/g .

Applying both technologies we've produced large industrial lots of material on the basis of intermetallic compound LaNi_5 .

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QUANTITATIVE APPLICATION OF LATERAL FORCE MICROSCOPY FOR CARBON NANOTUBES INVESTIGATION

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Abstract. Quantitative measurements of lateral force required for displacement of SWNTs bundle on the surface of highly oriented pyrolytic graphite with the help of atomic force microscope (AFM) were performed “in real time”. New method of quantitative calibration of lateral forces was used for interpretation results of lateral force microscopy (LFM). It allows us to receive numerical values of adhesion force of bundle to substrate easy and without specific equipment.

Keywords: Carbon nanotubes, Lateral force microscopy, Atomic force microscopy.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have aroused more and more research interest because of their unique structures and novel mechanical and electronic properties [2]. Single-walled carbon nanotubes (SWCNTs) are one-dimensional conductors or semiconductors, depending on their diameter and helicity, and native defects or localized distortion of the lattice induced by artificially bending can greatly change the transport properties of SWCNTs [3]. The outstanding electronic properties together with nanoscale size and high strength and flexibility, make SWCNTs the ideal building block for nanotechnology and nanoelectronics. New quantum electronic devices based on CNTs have been demonstrated recently [4, 5]. But fabrication of functional devices based on nanotubes is still a great challenge.

Atomic force microscopy [6, 7] is one of the most suitable methods for research carbon nanotubes. AFM allows to receive not only a relief of the studied sample, but also distribution of mechanical characteristics, electric, magnetic and other properties on its surface. With the help of AFM, controllable manipulation of individual CNTs and CNTs bundles became possible. In this paper we report our approach to manipulating SWCNTs bundles with lateral force microscopy. LFM gives possibility to study lateral forces that probe acts upon bundles. In spite of good visualization of LFM, its lack is absence of reliable techniques of quantitative interpretation of results. The new way of calibration developed ourselves has allowed to pass from qualitative estimations to quantitative investigations [8]. The given calibration technique is much more exact, than others known till now [9, 10], and does not assume simplification. With the help of new technique we may study adhesion of bundles to substrate and adhesion of CNTs in bundle qualitatively “in real time” more easy way. This result will provide new possibilities for nanotube application.

2. The description of experiment

The equipment and a method of research. Research was made on an atomic force microscope NTegra (NT-MDT, Russia). Silicon cantilever CSC12(B) (Micromasch, Estonia) was used. Radius of silicon tip was about 60 nm.

In LFM the sample is scanned in a contact mode in a direction perpendicular to axis of cantilever. Lateral force twists a beam. Twisting angle is registered by optical system (Fig. 1). The laser beam, being reflected from the top surface of cantilever, comes on a four-section photodetector which generates signals DFL and LF, depending on displacement of a light spot in two mutually perpendicular directions. Thus, signal DFL corresponds to a vertical bend of a beam of cantilever, and signal LF corresponds to the twisting caused by lateral forces.

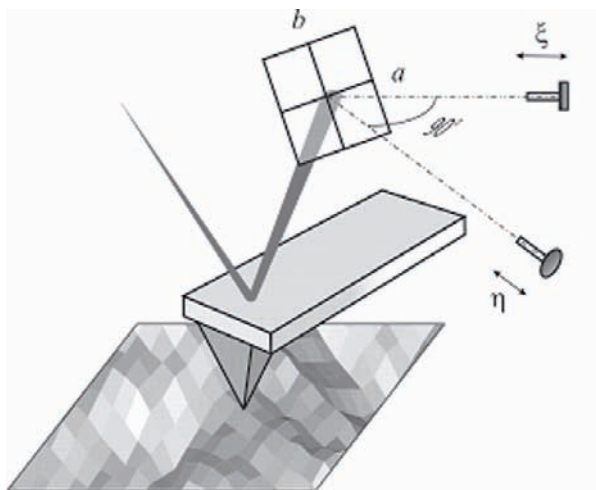


Figure 1. The scheme of optical system of registration of a microscope.

The sample. Single-walled opened carbon nanotubes have been provided by Dr. V.E. Muradyan (Institute of Problems of Chemical Physics of the Russian Academy of Science). Nanotubes have been synthesized by the arc discharge [11]. Their initial length made up 5-10 microns, diameter made up 1.5 nanometers. Then they have been milled in a solution of nitric and sulfuric acids during 12 hours. After washing of carbon nanotubes powder was dispersed in ethyl alcohol. A final spirit solution contains 1/10 part of nanotubes. The drop of solution has been placed on a surface of highly oriented pyrolytical graphite (HOPG). After alcohol evaporation nanotubes (single and grouped into bundles) were besieged on a surface of the sample. Namely bundles of nanotubes also became object of research in the given work.

According to our measurements, average diameter of single nanotubes is 1.5 nanometers, height of bundles is up to 100 nanometers (below the bundle with height of 40 nanometers is considered).

Experiment. The sample was scanned in a direction crossing a bundle of nanotubes. The gradient maps represented at Fig. 2a, 2b show relief of a bundle and

distribution of signal LF received by LFM correspondingly. Their cross-sections along the particular scanning line are demonstrated at Fig. 2c, 2d. The purpose of experiment was studying influence of external lateral action on a bundle of nanotubes. AFM allows to control magnitude of such action by change of normal load exerted on the bundle by the AFM tip.

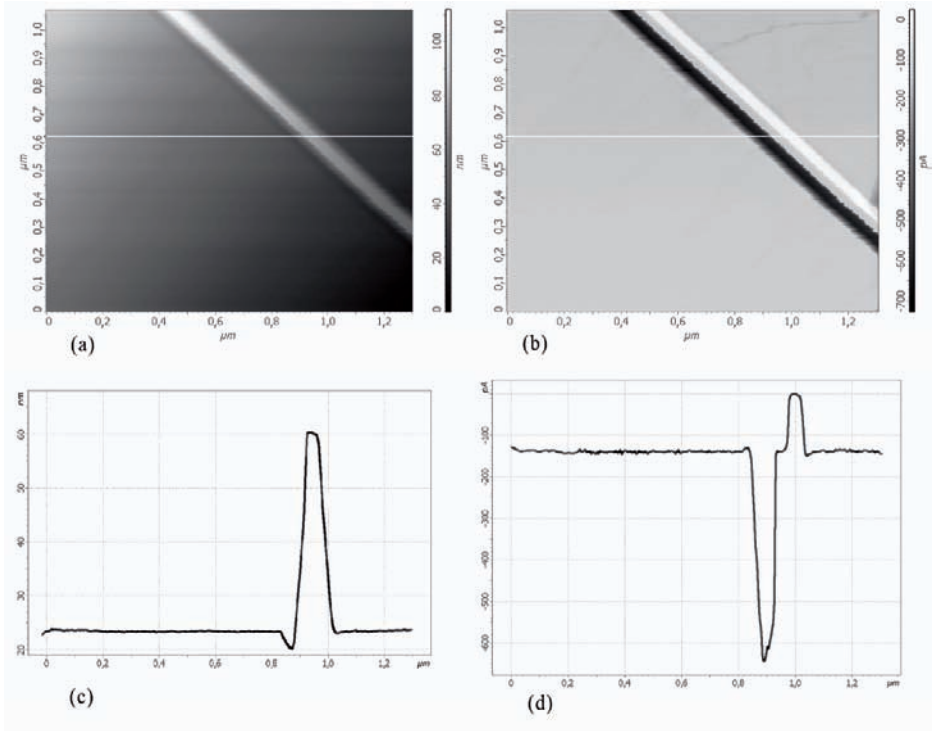


Figure 2. Relief (a), LF signal distribution (b), and corresponding cross-sections along the white line (c), (d). Constant line slope was subtracted in (c).

The manipulation procedure followed several steps. First, the surface was imaged in a standard way in contact mode, the bundle and the manipulation area were selected. Then we began scanning the selected area with the same normal load (1.3 nA in terms of photodetector's currents). Each line was scanning twice – from left to right and in reverse direction. At the particular line scanning was paused and further scanning was along this line only without interline displacement until the end of experiment. Thus, one observed continuously the same cross-section of the bundle “in real time”. This way we spied both normal load and lateral force profiles.

Then we increased step by step normal load by lifting the surface towards the tip. So the lateral force acted upon the bundle become monotonically greater too. Dramatically changing of observed profile mean bundle displacement or other critical event likes bundle splitting or destruction. Afterwards the tip-sample

distance was restored to the normal imaging conditions and scanning was continued all over the investigated area to look at the result bundle configuration.

To spy normal load and lateral force profiles we output on a computer monitor DFL and LF signals correspondingly and appended data file with their numerical values. Normal load was increased as rapid as 0.042 nA/sec (0.82 nN/sec) in terms of photodetector’s currents. The part of this trend is demonstrated at Fig. 3. One can see linear growth of load from 25 nN to 240 nN (we varied the load from 1.3 to 12.1 nA, but only the most interesting part is represented). Peaks of signal on border of bundle are artifacts caused by inertia of feed back loop. Simultaneously lateral force represented at Fig. 3 on the flat places of the sample (out of the bundle) raised too. There are two peaks per scanning cycle at the last graph. It means that the probe convoluted over the bundle and absolute value of lateral force abruptly increased. After 9 seconds at Figure 3 several peaks were disappeared so we obviously acknowledged some critical event. For examination result and to analyze what was happened with bundle of nanotubes scanning was restored with original value of load for relief imaging. Looking at Fig. 4 one can understand that bundle displaced as a solid body without any deformation. The images received are reliable and well seeing nanotubes displacement is real and is not due.

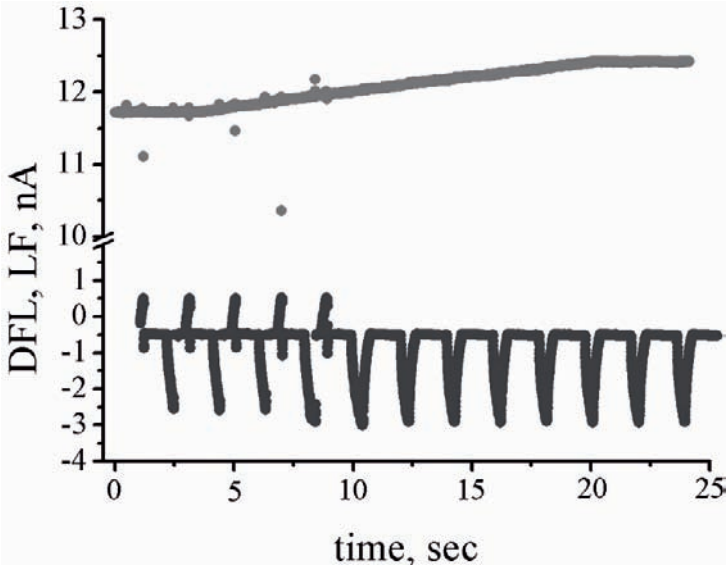


Figure 3. Oscillogramm of DFL and LF signals “in real time”. Displacement of DFL and LF with respect to each other concerns with operator’s lag effect.

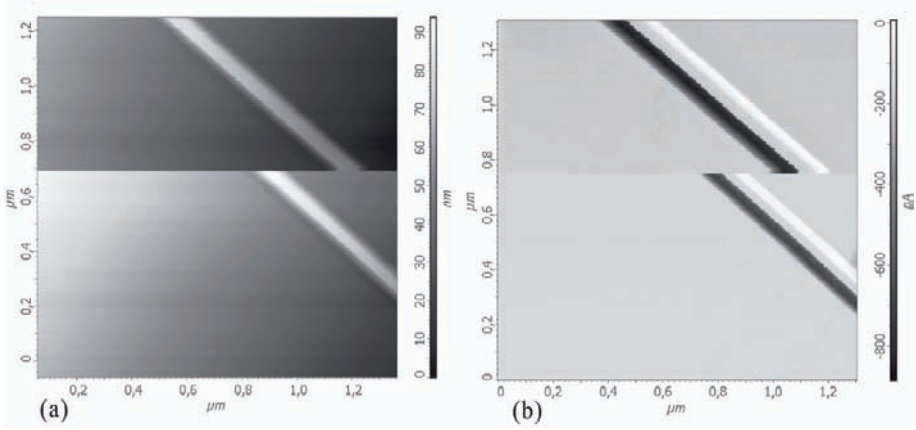


Figure 4. Examination of manipulation result.

3. Quantitative interpretation of results

To define absolute value of force acted during the experiment we need recalculate DFL and LF signals measured in nA into normal load force and lateral force using natural force units (nN). Method of normal load calibration is well known:

$$F_N = k_N \frac{dz}{dDFL} DFL, \quad (1)$$

where k_N – normal force constant of cantilever, $\frac{dz}{dDFL}$ – slope of linear part of

force-distance curve, $DFL = DFL(\text{feed back on}) - DFL(\text{feed back off})$. In our case $k_N = 2.1 \text{ N/m}$ (it was determined by Sader's method [12]), $\frac{dz}{dDFL} = 9.3 \frac{\text{nm}}{\text{nA}}$, so

$\frac{F_N}{DFL} = (19.5 \pm 2.0) \frac{\text{nN}}{\text{nA}}$. Using Fig. 3 we find that normal load when bundle displacement occurred was equal $(240 \pm 24) \text{ nN}$.

Calculation of the critical lateral force is more complicated because traditional LFM does not provide us with easy method to translate current units into force ones. There is no way to define the factor of proportionality until calibration algorithm was developed recently by ourselves [8]. The required coefficient depends on design of a microscope, adjustment of the optical system, torsion force constant k_L of cantilever and tip height l_{tip} .

To determine torsion force constant and height of tip we didn't refer to cantilever passport parameters that can be significant varied. The value of k_L we found used new the most precise method based on analyzing of amplitude-phase characteristic [to be published] but tip height was determined with the help of optical microscope. We got $k_L = 77.1 \text{ N/m}$; $l_{tip} = 10 \text{ }\mu\text{m}$.

Then in accordance with our method we did special manipulations with photodetector and produced some additional measurements. We got finally calibration factor $\frac{dF_L}{dLF} = (5430 \pm 540) \frac{\text{nN}}{\text{nA}}$.

As LAT signal and force proportionality was known we determined critical lateral force caused displacement of the bundle. The maximum absolute value at the graph (Fig. 3) just before critical event should be interpreted as finding value. It estimates $(14.1 \pm 1.4) \mu\text{N}$.

4. Conclusions

Methods of AFM, by means of a new method of calibration of lateral forces, allow to quantitatively investigate various mechanical characteristics of nanotubes. We have demonstrated one of applications of this method and determined critical lateral force that displace bundle of nanotubes over HOPG surface. The advantage of the work is possibility of “real time” observation of moment of nanotubes displacement, so relatively exact value of the lateral force caused such event can be estimated.

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THE CORRELATION BETWEEN IONICITY OF METAL-HYDROGEN BONDS IN HYDRIDES AND THEIR THERMAL FIRMNESS

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Abstract. The information obtained by the X-ray absorption spectroscopy method about the process of charge transfer from atoms of metal to hydrogen atoms in metal hydrides of 111, 1Y groups and in hydrides of intermetallic compounds of AB and AB₅ composition has been used to determine correlation between thermal stability of mentioned hydrides and the degree of ionisity of their Me-H bonds. A supposition, that found out correlation reflects the dependence of height of activation barriers of the process of associative desorption of hydrogen in hydrides from the value of transfered charge to hydrogen, i.e. the value of ion component Me-H bonds of hydrides has been made.

Keywords: hydrides, metal-hydrogen bonds, thermal stability, X-ray absorption spectra

1. Introduction

The connection between plateau pressure of isotherm, thermal stability of hydrogen-contained phase with such geometrical adjectives of its crystal structure as unit cell volume, the size of interstitial pores, distance between atoms of lattice has been determined by numerous scientists. As geometrical adjectives of unit cell are closely connected with characteristic of electron structure of hydride phase [1-5], the existence of connection of thermal stability (and pressure of plateau) of metal-hydride with characteristics of its electron structure can be expected too, for example, with nature of metal-hydride bonds in hydride, with the quantity of transferred charge from metal atoms to hydrogen atoms (and vice versa). One of these bonds has been determined by us at investigation of electron structure of hydrides of IV -group metals and intermetallic hydrides of AB and AB₅ composition by the X-ray absorption spectroscopy method [6-8]. By the direct X-ray spectrum analysis [9] according to the shift of absorption spectrum of metal-components of hydride forming compounds at the transition to their hydrides the correlation between the value of transferred charge from metal to hydrogen and the value of equilibrium, corresponding to the isotherm plateau, pressure, thermal stability of hydride has been established. We can conclude that correlation between the ionicity of metal-hydrogen bonds in the hydrides investigated and their hydride-desorption and thermodynamic properties have been found. This correlation can have both scientific and practical interest. It allows to understand better the mechanism of reduction of thermal stability of metal-hydrides by their mechanical alloying [10], and can be useful in the search of the most efficient way of reduction (or

increasing) of thermal stability of hydrides in practical demand and hydrides which are not widely used because of their high thermal stability (magnesium hydride).

2. Experimental results, pointed out the correlation existence

As a result of carried our experiments we can note that metal-hydrides which equilibrium pressure at ambient temperature is close to atmospheric and which have low thermal stability and dissociate at rather low temperatures, show practically full lack of ionic part of metal-hydrogen bond, the latter were of covalent or covalent-metallic character. X-Ray investigation of $\text{TiFeH}_{1.8}$ and $\text{LaNi}_5\text{H}_{6.9}$ metal-hydrides, which are widely used nowadays, prove this. In fact, we can see in Fig. 1 a,b, that at the transition from TiFe to $\text{TiFeH}_{1.8}$ there is no shift of K-absorption spectra of titanium and iron within the limits of error[6]. It testifies that titanium and iron have the same charge state in intermetallic compound and its hydride and allows to say that hydrogen atoms at formation of Me-H bond do not give any visible part of the charge to titanium and iron. It means that there is practically no ionic component of metal-hydride bonds in $\text{TiFeH}_{1.8}$ hydride. At the same time this hydride has the equilibrium pressure close to atmospheric and low dissociation temperature.

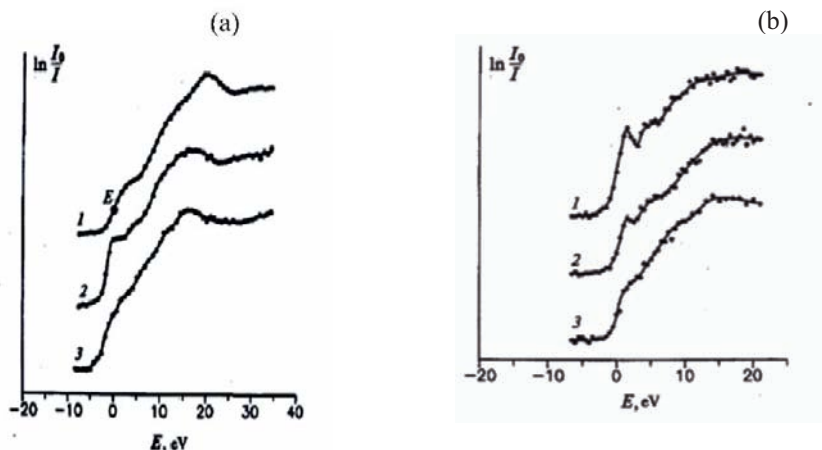


Figure 1. K-absorption spectra of Fe (a) and Ti (b) in metal – 1, TiFe – 2, $\text{TiFeH}_{1.8}$ – 3.

At $\text{LaNi}_5\text{H}_{6.9}$ hydride formation the charge state of nickel and lanthanum atoms practically does not change and is the same as in LaNi_5 . Practically the same position of point “A” on the curves of K-absorption spectra of nickel in LaNi_5 and $\text{LaNi}_5\text{H}_{6.9}$ and on the curves of L_{111} - absorption spectra of lanthanum in these compounds shown in Figs. 2,3 testify that. This result allows to ascertain the lack of charge transfer from lanthanum and nickel atoms to hydrogen atoms at $\text{LaNi}_5 \rightarrow \text{LaNi}_5\text{H}_{6.9}$ transition and to say about the lack of ionic component of La-H and Ni-H metal-hydrogen bonds and to characterize these bonds as essentially covalent or covalent-metallic as well. We must confirm that $\text{LaNi}_5\text{H}_{6.9}$ hydride as well as studied $\text{TiFeH}_{1.8}$ hydride decomposes at low temperature and its equilibrium pressure at ambient temperature is close to atmospheric.

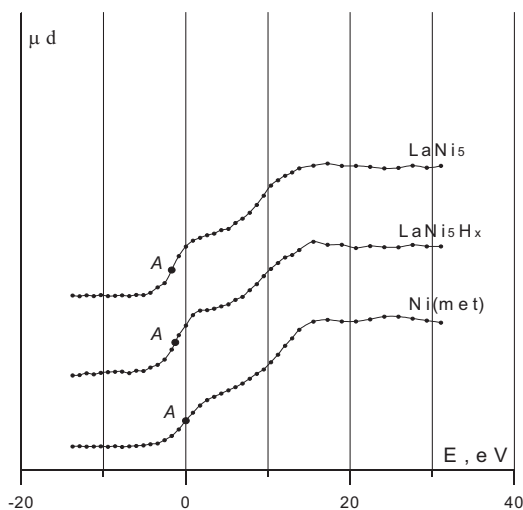


Figure 2. K-absorption spectra of Ni in metal, LaNi₅ and LaNi₅H_x (x=6,9).

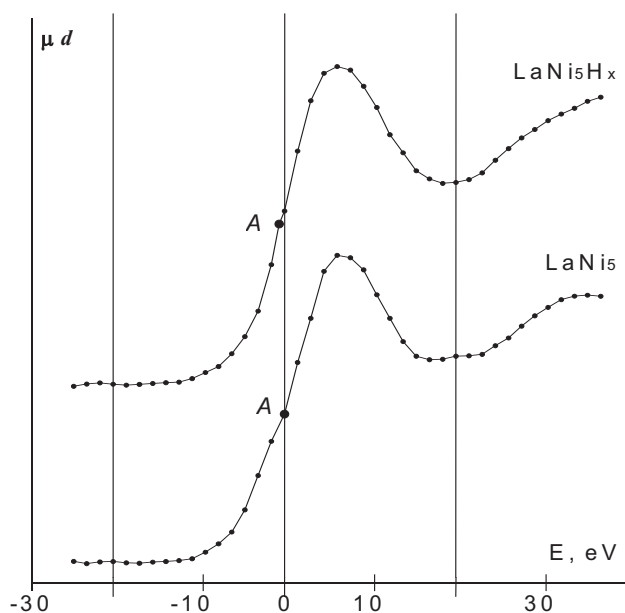


Figure 3. L₁₁₁-absorption edges of La in LaNi₅ and LaNi₅H_x (x=6,9).

The data on character of chemical bonds in binary hydrides of Ti, Zr, Hf [7] obtained by us by X-Ray absorption spectroscopy method testify about the existence of correlation between the degree of ionicity of Me-H bonds in hydrides

and their thermal stability. Titanium-hydrogen bonds in $\text{TiH}_{1.83}$ hydride, which thermally more stable than $\text{TiFeH}_{1.8}$ and $\text{LaNi}_5\text{H}_{6.9}$ and its decomposition temperature is higher than 500°C , and its equilibrium pressure at ambient temperature is lower than atmospheric, cannot be estimated as pure covalent bonds according to X-Ray results (Fig. 4). Taking account of 0,9eV shift of K- titanium absorption edge of $\text{TiH}_{1.83}$ comparing with its position in metallic titanium, we can make a conclusion about the transmission by titanium atoms part of their covalent electrons to hydrogen atoms, i.e. about partly ionic character of Ti-H bonds, which have mainly covalent character. The same conclusion can be made at analysis of the character of Me-H bonds in hydrides of Zr and Hf.

The sensitivity of X-Ray absorption K-spectra of titanium and iron to variation in the charge state of the atom is not the same[6]. It is higher for the iron K-edges. The curves in Fig. 5 clearly demonstrate that, in accordance with Kunzl's rule, a larger energy shift of the iron K-edge is observed in the compound with a greater valency of iron, namely 10 eV in FeSO_4 and 14 eV in Fe_2O_3 . A considerable shift of the iron K-edge in going from pure metal to the compound FeSO_4 (10 eV), that is when the iron atom goes from state Fe^0 to state Fe^{2+} , points to very high sensitivity of the method to charge transfer, especially if one takes into account that the error in determining the energy position of specific points in the absorption curve is 0,2 eV. The titanium absorption K-edge is shifted by 12,3 eV in going from metal to oxide TiO_2 (Fig. 4), i.e. when titanium atoms change over from metallic Ti^0 to four-valance state Ti^{4+} . However, even this sensitivity of the titanium absorption K-edges is sufficient to reveal a change in the charge state of titanium atoms of the order of 0,1 of electron charge.

The obtained by us and represented in Fig. 6, K- absorption spectrum of yttrium in its hydrides showed that we can talk in this case about existence of connection between thermal stability of yttrium hydride and quantity of ionic constituent in its metal-hydride bonds, if thermal stability is judged by the temperature of beginning of intensive decomposition of hydride phase, and ionic constituent of Me-H bond is estimated by the quantity of shift of K-edge of absorption spectrum of yttrium in hydride relatively the same edge of absorption spectrum of metal yttrium. Our carried out experiments on thermal desorption of hydrogen show that YH_2 is more thermally stable than YH_3 . At the same time K-edge of yttrium in YH_2 is much shifted to the area of higher energies, than K-edge of yttrium in YH_3 (Fig. 6(b)), relatively the edge of absorption spectrum of metal yttrium, that testifies about larger ionic constituent of Me-H bonds for this hydride than for YH_3 hydride. As evident from the experiment, to larger thermal stability of hydride is corresponded the higher degree if ionicity of its metal-hydride links and, consequently, the results of this X-ray spectrum analysis of yttrium hydrides testify about the existence of mentioned above correlation.

K-absorption spectrum of yttrium in YH_3 , which was mechanically treated in a ball planetary mill during 20 min. with angular rate of 1630 rot./min. is shown in Fig. 6 (c). This absorption spectrum, as seen from the picture, is shifted relatively to the spectrum of untreated YH_3 hydride to the side of lower energies, which in accordance with the found out correlation has to testify to thermal stability of reduction of treated yttrium hydride. Actually, we determined by the method of hydrogen thermal desorption, that as a result of mechanic dispersing of this hydride its temperature of decomposition decreased more than on 300°C (Fig. 7), i.e. the

reduction of its thermal stability took place, and absorption spectrum of yttrium responded to it by the shifting to the side of lower energies (Fig. 6 (c)).

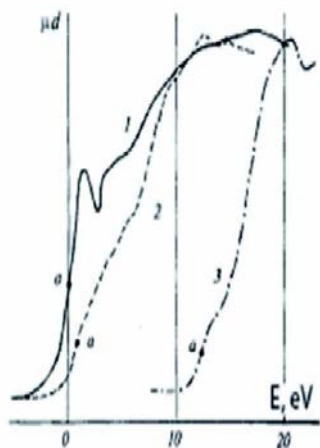


Figure 4. K-edges of Ti in metal – 1, TiH_2 – 2, TiO_2 – 3.

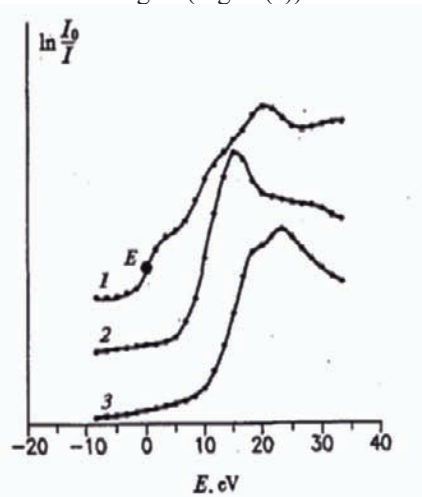


Figure 5. K-edges of Fe in metal – 1, FeSO_4 – 2, Fe_2O_3 – 3.

Therefore, X-ray absorption spectrums, having information about character of Me-H bonds in metal-hydrides, can be used for studying influence on their thermal stability of different factors and processes.

3. About the nature of found out correlation

What is the mechanism of influence on the temperature of hydride decomposition of charge state of hydrogen ion and metallic ion of matrix? To answer this question we have to estimate on what stage of known mechanism of hydrogen decomposition this influence can be the most sufficient. We think it may be both at the stage of hydrogen leaving from the volume of lattice into the surface and, especially, at the stage of transition of atomic hydrogen which came into the surface into the gas phase, as a result of its associative desorption with the formation of molecular hydrogen. Let us examine as an example the split of binary hydride on pointed stages in two cases: in the assumption of pure covalent (or covalent-metallic) and pure ionic character of its Me-H bonds. Take into account that temperature of hydride decomposition should be connected not with energy of Me-H bond itself but only with the depended on their character (covalent or ionic) the height of overcoming potential barrier by atoms or ions of hydrogen on their way from volume to the surface and at leaving beyond for approaching and association, the energy of the former passes to the lattice for Me-H bond opening. We think that at the assumption of covalent Me-H bonds, to the simultaneous leaving beyond the lattice of two electrically neutral (at any moment) quasi-atoms of hydrogen for their approaching and association, neutral quasi-atoms of metal will show less resistance than for pure ionic Me-H bonds, when to such

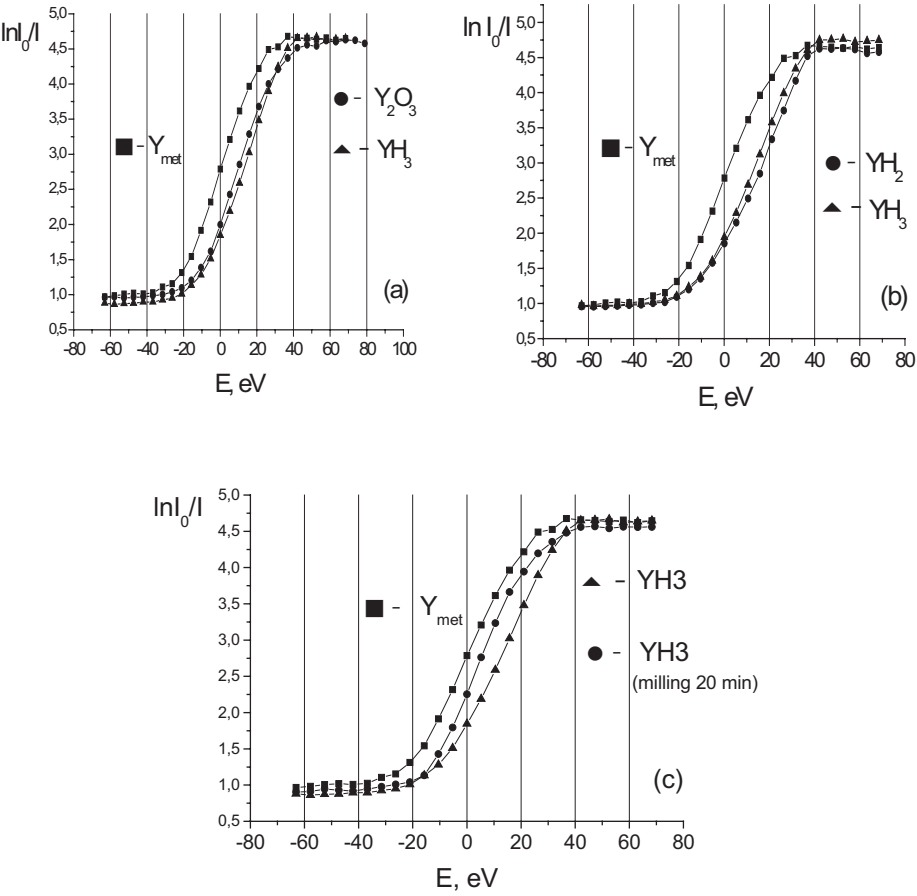


Figure 6. K-edges of yttrium in metal and compounds: (a) - Y_2O_3 , YH_3 ; (b) - YH_2 , YH_3 ; (c) - YH_3 and YH_3 after milling 20 min.

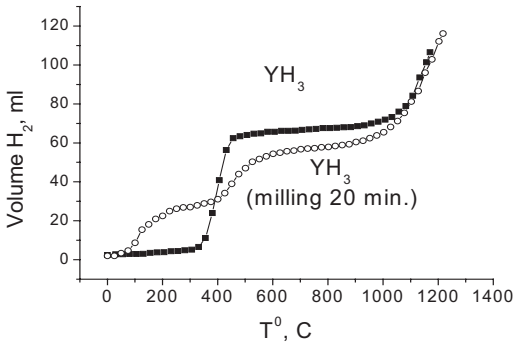


Figure 7. The thermodesorption curves (at $P=0,1$ MPa) of yttrium hydrides before and after mechanical dispersion.

simultaneous leaving beyond the lattice of two hydrogen ions and their following approaching and assimilation from the side of metal ions the restraining force of their Coulomb interaction will hinder. To overcome created by this force potential barrier it is necessary to increase the temperature of hydrogen heating, and the more increase the more charge of hydrogen ion is, i.e. the more ionicity degree of Me-H bond. At the stage of hydrogen migration from the volume to the surface of the lattice the relative height of overcoming potential barriers at the case of covalent character of Me-H bonds in comparison with the case of pure ionic bond, we consider, will be lower too, as covalent bond on the all way from the volume to the surface is capable to support neutral charge condition of moving hydrogen atom, and therefore more lower that for pure ionic bond the height of barriers, to overcome which we need lower temperature of hydride heating. It is necessary to pay attention to one peculiarity of hydrogen-metal interaction. Unlike carbon, for example, hydrogen is unable to form with several neighbours simultaneously direct covalent bond. It causes, from our point of view, peculiar to hydrogen special, practically without-barrier, in many cases, character of moving in different directions inside the lattice of metal at the room temperature and explains besides this, anomalistically enormous mobility of hydrogen in comparison with carbon and nitrogen.

We can conclude from the carried out investigation of hydride splitting, that in the case of mixed character of Me-H bonds in the frames of examined simplified model we can expect the more higher temperature (and thermal stability) of hydrogen decomposition the more degree of ionicity of its Me-H bonds is. Consequently, by choosing alloying elements which influence on the character of chemical hydrogen-metal bonds in hydrides, we have a possibility to change their thermal stability.

4. Conclusions

It should be concluded, that study by the method of X-Ray absorption spectroscopy of charge transformation at metal-hydrides formation, the role of hydrogen ion charge at the process of formation of their hydrogen-sorption, thermodynamic and electron properties allows not only to understand the chemical nature of these compounds, but establish the connection between different hydrides properties, for example, electron and thermodynamic, study mechanism of influence of one properties on other. Thus, purposively changing electron properties, character of chemical bonds by alloying, we can change their hydrogen-sorption and thermodynamic properties and solve different practical and technological problems.

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ABOUT MANNER AND MECHANISMS OF REDUCTION OF THERMAL FIRMNESS OF Mg -, Ti -, Y – BASED MECHANICAL ALLOYS

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Abstract. The influence of mechanical grinding and alloying due to high energy ball milling upon the decomposition temperature and thermal stability of hydride phases of systems Ti-B-H, Y-H, Mg-Fe-H have been investigated. It was established that, decomposition temperature of grinding $TiH_{1.9}$, YH_3 , MgH_2 is lower as compared the initial hydrides. The redistribution of hydrogen after high-energy influence took place: the part of weak- and middle-bounded hydrogen increased but part of strong-bounded hydrogen decreased and the more the dispersion degree higher. It was established that, addition of boron reduces thermal stability $TiH_{1.9}$ more, than on $300^{\circ}C$; addition on 10 wt. % of Fe to Mg contributes to higher dispersion degree. The instruction of the hydride phases processes of the powder Mg and Mg + 10wt. % Fe derived in the conditions of high-energy ball-milling in hydrogen under pressure of 1.2 MPa have been studied. The thermal firmness of MgH_2 formed at this treatment more than on $100^{\circ}C$ decreased. Mechanisms of influence alloying and of dispersion on thermal stability of hydrides have been studied.

Keywords: mechanical alloying, grinding, thermal stability, hydrides

1. Introduction

The obtaining of new hydride phases based on Mg, Ti, Y with low temperature of decomposition is a burning problem nowadays. Well-known hydrogen-capacious hydrides of MgH_2 (7.6 wt.%), YH_2 (11.2 wt.%) and YH_3 have high thermal stability and it prevents them from wide using as hydrogen accumulators. Titanium hydride TiH_2 has high temperature of decomposition too. As this hydride is actively used at different material syntheses it is very important to decrease its temperature of decomposition.

One of new methods of magnesium, transition and rare-earth metals hydrides and their compounds obtaining is mechanical-chemical method. Numerous quantity of works are devoted to the improving kinetic, sorption properties of hydrides which were treated mechanically or were obtained by this method in hydrogen medium under pressure [1-7]. Great consideration is given to the influence of dispersity on phase equilibrium. At the same time the investigation of mechanical

grinding, alloying on temperature of hydrides dissociation is practically lacking [8,9].

In represented work the influence of mechanical dispersing and boron and iron alloying on thermal stability and temperature of decomposition of hydride phases of mechanical alloys (MA) of Ti-B-H, Y-H and Mg-Fe-H systems have been investigated by the methods of thermal desorption of hydrogen (TDH), X-Ray analysis, scanning electron microscope method (SEM). The mechanisms of thermal stability decreasing as a result of grinding and alloying has been investigated as well.

2. Experimental details

Powders of MgH_2 , $\text{TiH}_{1.9}$ and YH_3 hydrides, obtained from the gas phase, were mechanically grinded. Grinding was carried out in a ball planetary mill in argon medium at rotation speed of 1630 rot/min. Grinding balls and hydride bulk were in ratio of 20:1.

Mechanical alloying of MgH_2 with iron and $\text{TiH}_{1.9}$ with boron was carried out in ball planetary mill too. To find out the role of boron in the decreasing of thermal stability of $\text{TiH}_{1.9}$ mechanical alloys from ($\text{TiH}_{1.9} + 40 \text{ wt.\% B}$), ($\text{TiH}_{1.9} + 50 \text{ wt.\% TiB}_2$) mixtures were obtained. The duration of mechanical treatment was 20 min at the same conditions as for $\text{TiH}_{1.9}$ hydride, which was the comparative object. Mechanical treatment of ($\text{TiH}_{1.9} + 9 \text{ wt.\% B} + 13 \text{ wt.\% Ti}$) mixture lasted 50h. Such duration was chosen to rich maximum total effect of reduction of temperature hydride titanium decomposition as a result of its grinding and alloying.

It was shown by x-Ray analysis of mechanical alloy, obtained by treatment of $+(\text{TiH}_{1.9} + 40 \text{ wt.\% B})$ mixture that on the pattern there are diffraction lines of the same phases as for the initial mixture – titanium hydride and boron, but the lines of these phases are considerably wider, it is the cause of mechanical grinding of particles and appearing of considerable quantity of defects in them. Beside this there are TiB and TiB_2 traces. We can conclude from analysis of diagram of this mechanical alloy that mechanical treatment of ($\text{TiH}_{1.9} + 40 \text{ wt.\% B}$) mixture during 20 min does not lead to the changing of the main phase composition, that is decomposition or phase transformation with structure changing one of the components is not observed. All the same is for MA, obtained by the treatment of ($\text{TiH}_{1.9} + 50 \text{ wt.\% TiB}_2$) mixture during 20 min. We can see the same lines on the pattern of this MA (Fig. 1b), as for initial mixture – titanium hydride and TiB_2 . X-ray diffraction spectrum of the sample of ($\text{TiH}_{1.9} + 9 \text{ wt.\% B} + 13 \text{ wt.\% Ti}$) mixture after 50h of grinding, is a wide line reminding in its shape “galo” from amorphous structure being surrounded with the set of wide and weak-intensive reflexes (Fig. 1c, curve 2). We can say that pattern of this MA considerably differs from the pattern of initial mixture of this alloy (Fig. 1c, curve 1) and is typical for superdispersed powders picture of superposition of a great quantity of rather wide and overlapping diffraction reflexes. We can conclude that treated mixture of ($\text{TiH}_{1.9} + 9 \text{ wt.\% B} + 13 \text{ wt.\% Ti}$) composition is multiphase. The composition of the former differs from the composition of the one before treatment. We can find reflexes on the X-ray picture of TiH_x and TiO , and TiB , TiB_2 compounds formed as a result of high-energy influence on Ti and B. But all of these compounds because of the fuzziness of

spectrum were identified only by one or two diffraction lines, belonged to each of the pointed compounds.

The processes of hydride formation at high-energy mechanical treatment in hydrogen media under pressure of 1.2 MPa were investigated on pure magnesium powders and on Mg + 10 wt.% Fe powders mixture. Powder of pure magnesium was been treated during 3 hours, whereas Mg + 10 wt.% Fe during 1 and 5 hours. Initial powders of Mg and Fe (purity 99.9%) had average particle size of 3.2 and 10 μm correspondently. Pure hydrogen was given into the reaction chamber of the ball miller from a metal-hydride accumulator every 30 min. of grinding to keep pressure of hydrogen in the chamber equal to 1.2 MPa.

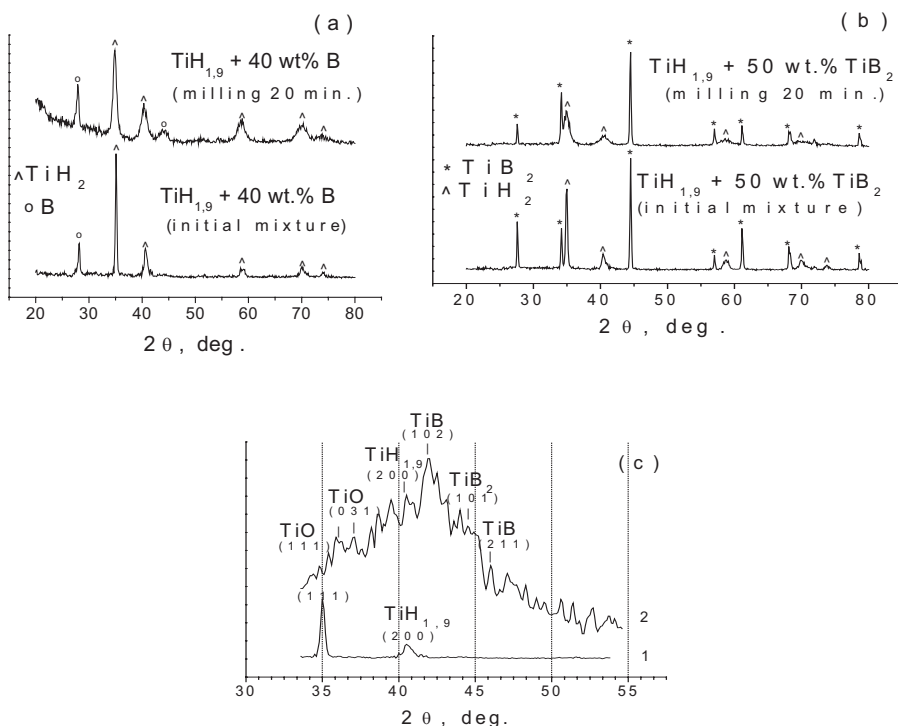


Figure 1. X-ray diffraction patterns of MA prepared by mechanical grinding for 20 min:

- (a) $\text{TiH}_{1.9} + 40 \text{ wt.\% B}$, (b) $\text{TiH}_{1.9} + 50 \text{ wt.\% TiB}_2$;
- (c) $\text{TiH}_{1.9} + 9 \text{ wt.\% B} + 13 \text{ wt.\% Ti}$ for 50h.

The processes of hydride formation at high-energy mechanical treatment in hydrogen media under pressure of 1.2 MPa were investigated on pure magnesium powders and on Mg + 10 wt.% Fe powders mixture. Powder of pure magnesium was been treated during Thermal decomposition of all the specimens was carried out in a glass-quartz plant of Sieverts type in hydrogen medium at atmosphere pressure. The plant provided even heating with the rate of 1°/sec and automatic registration of curve of dependence of quantity of released hydrogen at hydrides decomposition from their temperature (thermal desorption curves).

X-ray analysis of specimens before and after grinding has been carried out on the automatic complex on the base of DRON-3M in Cu $K\alpha$ -beaming with the graphite monochromator.

Changing of powders surface of investigated mixtures as a result of their mechanical treatment has been estimated by specific surface measuring by the BET method.

3. Results and Discussion

As during the mechanic synthesis processes of alloying and grinding take place simultaneously and as a result we have the total effect of their influence, firstly some experiments on finding possibility of thermal stability reduction of unalloyed hydrides of Ti, Y and Mg as a result of mechanic grinding only have been carried out.

Mechanic grinding in planetary ball miller powders of unalloyed hydrides of Ti, Y, and Mg made particles size sufficiently smaller (their average size got smaller for titanium hydride from 12 to 0.17 μm , for yttrium hydride from 2 to 0.17 μm , for magnesium hydride from 3.3 to 0.6 μm). X-ray analysis showed that 20 min grinding did not lead to appearing new lines on X-ray pictures of treated specimens which pointed to changing of phase composition. The same lines for initial hydrides are considerably wider here. It is evidence of particles size changing and bringing numerous defects and lattice distortion as a result of dispersion and deformation.

The main result caused by the grinding is the substantial decreasing of temperature of hydrides dissociation – on 150° C for $\text{TiH}_{1.9}$, more than on 100° C for MgH_2 and on 300° C for YH_3 . It can be seen at comparing curves of hydrogen thermal desorption from pointed hydrides before and after grinding (Fig. 2). So we can say about decreasing temperature of decomposition, that is about decreasing hydrides stability being mechanically grinded.

The dynamics of thermal decomposition of $\text{TiH}_{1.9}$, YH_3 , MgH_2 hydrides (initial and after mechanical treatment during 20 min.) is shown in spectrums of hydrogen thermal desorption (curves of dependence of hydrogen release rate from temperature of the specimen) (Fig. 3). In $\text{TiH}_{1.9}$ hydrogen release spectrum we can see three picks of hydrogen release, showing the presence of three groups of hydrogen atoms: weak-bounded, average- and strong-bounded hydrogen. We have in mind that atoms of strong-bounded hydrogen are the least moving in hydride lattice in comparison with atoms of middle- and strong-bounded hydrogen, as are in more deep potential wells and take higher temperatures to get over potential wells at their migration from the volume of the lattice to its surface and for the activation the process of associative desorption of

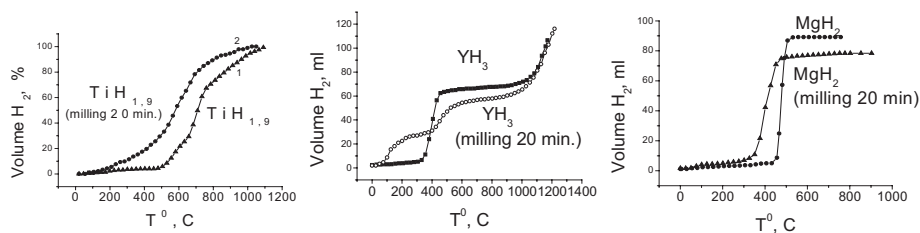


Figure 2. The thermodesorption of hydrogen curves (at $P=0,1$ MPa) of hydrides before and after mechanical dispersion.

hydrogen on the surface of crystal. It should be pointed out that we connect the temperature of hydrogen decomposition not with metal-hydrogen binding energy itself but only with the height of getting over potential wells, which depends on character (covalent, ionic) of these bonds, for example, of their ionicity degree [10]. In $\text{TiH}_{1,9}$ thermal desorption spectrum high temperature pick at 700°C should be connected with hydrogen which is in tetrahedral pores of titanium hydride cubic lattice. Pick at 550°C should be connected with grain boundary hydrogen and with hydrogen which is in areas with big tetragonal lattice distortions. Pick at 180°C can be connected with hydrogen adsorbed by the surface. Evidently, after high-energy influence on hydride and its dispersing the relative intensity of low temperature picks increased, i.e. part of weak- and average-bounded hydrogen. The redistribution of hydrogen took place. So dispersing at grinding leads to the widening of grain-boundary areas, formation of new surfaces and defects both on the surface and in the volume of crystal and as a result of this to the increasing of quantity of weak bounded and average-bounded hydrogen. The latter is accompanied by the increasing of free energy of dispersed particles, their thermodynamic potential that causes the decreasing temperature of hydride decomposition.

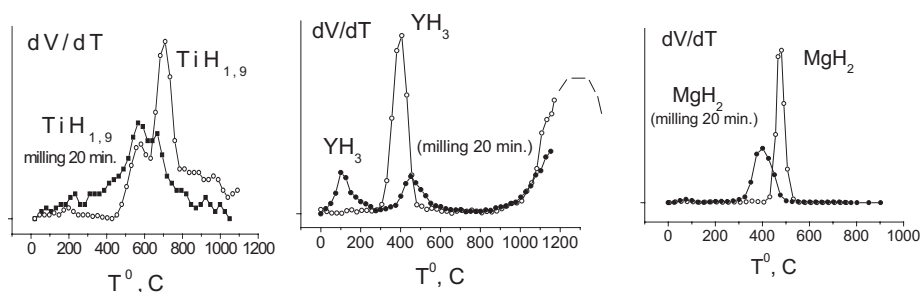


Figure 3. The thermal desorption spectra of hydrogen (at $P = 0,1$ MPa) of hydrides before and after mechanical dispersion.

Compare curves of hydrogen thermal desorption from mechanically treated mixtures of $\text{TiH}_{1,9} + 40$ wt.% B, $\text{TiH}_{1,9} + 50$ wt.% TiB_2 , $\text{TiH}_{1,9} + 9$ wt.% $\text{B}_2 + 13$ wt.% Ti with the curve of thermal desorption of non-treated $\text{TiH}_{1,9}$ (Fig. 4) we can see that mechanical alloying by boron additionally decreases the temperature of decomposition of dispersed $\text{TiH}_{1,9}$ hydride and maximum total effect of decreasing temperature of its decomposition is 300°C . Spectrums of thermal desorption of alloyed MA (Fig. 5) point to more active redistribution of hydrogen than from non-alloyed $\text{TiH}_{1,9}$ and it concerns more weak- and average-bounded hydrogen. We consider that mechanism of thermal stability decreasing in the case of boron alloying differs from the mechanism at dispersing: boron enters $\text{TiH}_{1,9}$ lattice influences on the charge condition of titanium and hydrogen atoms, and on the character of chemical link of Ti-H, which is mainly covalent in titanium hydride.

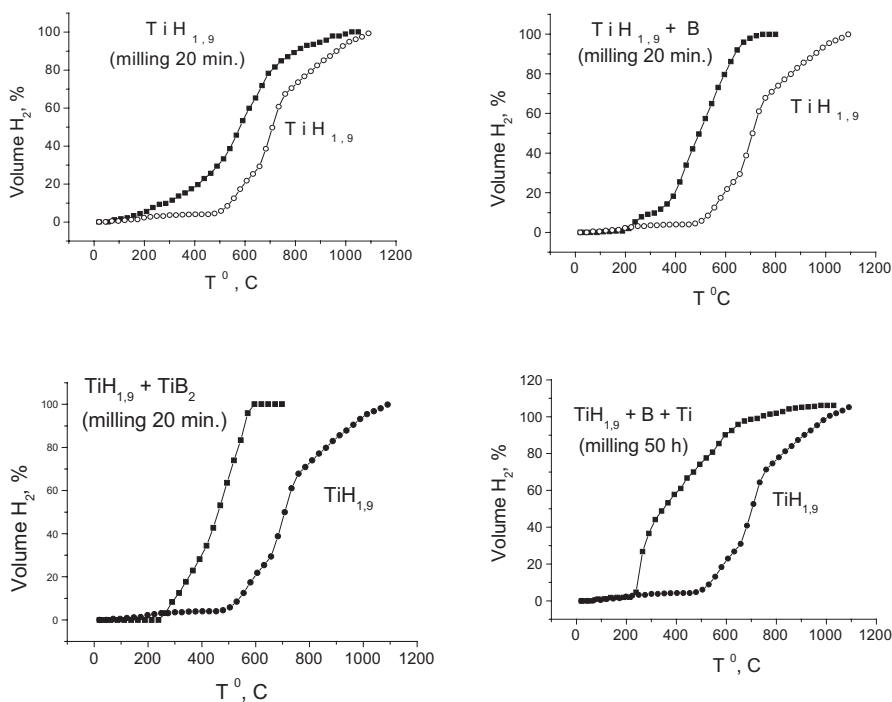


Figure 4. The thermodesorption of hydrogen curves (at $P = 0,1$ MPa) of hydrides after mechanical dispersion and alloying by boron.

High thermal stability of this hydride causes ionic component of Ti-H links. Boron, from our point of view, by decreasing positive charge on titanium atoms, decreases the ionic component of these links. That leads to the decreasing of hydride titanium thermal stability. Such mechanism of influence of alloying element - boron on thermal stability of hydride phase follows from the correlation between ionicity degree of metal-hydride links in hydride and its thermal stability having been founded out by us before [10]. Influence of dispersing and alloying of Fe on thermal stability of hydrogen phase of Mg-H system was studied on mechanical alloys of Mg + 10 wt.% Fe composition. Mechanical synthesis was carried out in metal-hydride hydrogen media under 1.2 MPa pressure. Magnesium powder was treated in the same conditions. X-Ray analysis showed that the formation of magnesium hydride takes place (up to 50 mass.%), metallic magnesium and iron traces were found too.

Microstructure of Mg + 10wt.% Fe mixture after dispersing during 1h. transforms into the layered particles without sufficient change of their size- from 3.5 μm initial to 4.5 μm . After 5h. of dispersing (Fig. 6.a) the average size of particles decreases to 0.2 μm . At the same time, for Mg without Fe adding after 3h. grinding (Fig. 6.b) we can see the conglomeration of particles, the increasing of average size of particles from 3.2 μm to 5 μm testifies it. That is presents of iron allowed to rich sufficient dispersing. It is in good accordance with works of authors [2] who showed that iron can be used as a dispersant.

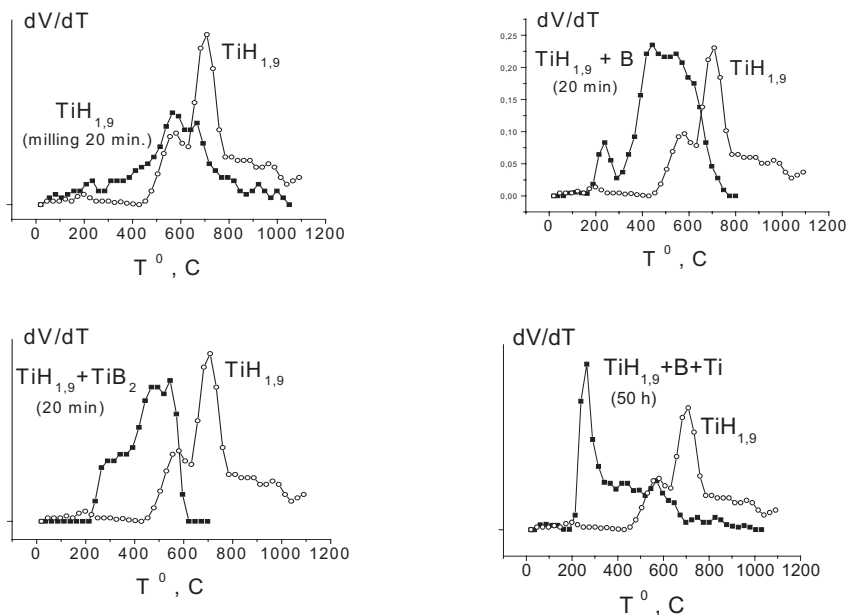


Figure 5. The thermal desorption spectra (at $P = 0,1$ MPa) of hydrides after mechanical dispersion and alloying by boron.

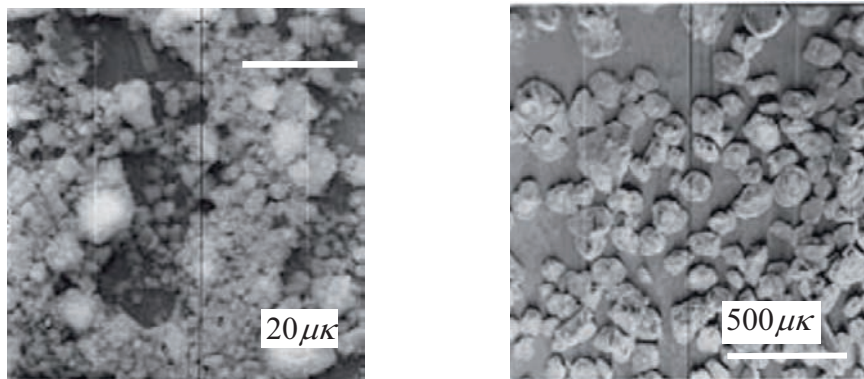


Figure 6. (a) – SEM micrographs of the microstructure of MA Mg+10 wt.% Fe after milling 5h under pressure 1,2 MPa in H_2 atmosphere.
(b) – the microstructure of Mg after milling 3h under pressure 1,2 MPa in H_2 atmosphere.

The decreasing of stability of hydride phase formed at mechanical treatment of Mg + 10wt.% Fe more than on $100^\circ C$ in comparison with hydride phase formed at treatment of Mg powder was established by thermal desorption method (Fig. 7). In spectrums of thermal desorption (Fig. 8) of hydride phase of alloyed MA three groups of hydrogen atoms were found too. Herewith the part of weak-bounded and average-bounded hydrogen in it exceeds the part of strong bounded hydrogen in comparison with unalloyed hydride phase. As for the full releasing of

weak-bounded and average-bounded hydrogen from metal-hydride lower temperature is necessary, it explains the decreasing of temperature of dissociation and magnesium hydride stability as a result of iron addition. We consider that besides such indirect influence can be direct influence of iron on thermal stability of MgH_2 . Iron as boron can influence the character of Mg-H chemical links by decreasing their ionic component and as a result thermal stability of hydride magnesium.

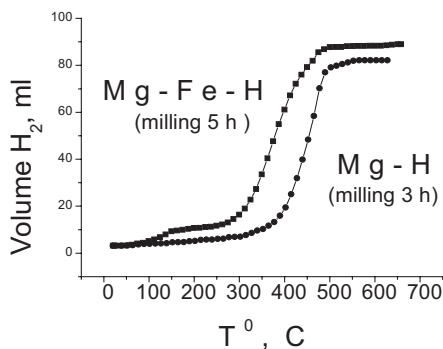


Figure 7. The thermodesorption of hydrogen curves of MA Mg+10wt.%Fe.

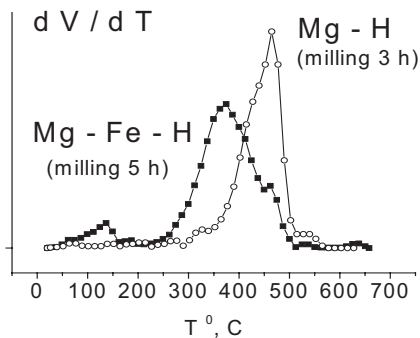


Figure 8. The thermal desorption spectrum of MA Mg+10wt.%Fe.

4. Conclusion

Carried out investigations of influence of grinding and alloying on thermal stability of hydride phases based on Mg, Y, Ti showed that chosen ways of decreasing of dissociation temperature and thermal stability of pointed hydride phases were sufficiently effective. Mechanisms of thermal stability decreasing as a result of dispersing and alloying by boron and iron have been investigated. It was shown the distinction of these mechanisms. It allows to formulate some principles of ruling of hydride phases stability and determine the ways of purposeful decreasing and if necessary increasing their temperature of decomposition.

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ELECTRONIC STRUCTURE AND STABILITY OF HIGHER FULLERENES

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Abstract. The structures of stable (i.e. produced, isolated and characterized) higher fullerenes have been analyzed. General rules governing the molecular structure of stable (extracted) higher fullerenes have been revealed. A number of fullerene substructures that have electronic features similar to their well known aromatic analogues have been identified. It has been shown, that the possibility of production of the isomers of higher fullerenes is defined by a position of the most energetically favorable isomer inside the suggested "beam of stability", constructed according to the calculated data for stable fullerenes, that the molecules have closed shell.

Keywords: fullerene, computational chemistry, chemical structure, electronic structure

1. Introduction

Stability of fullerenes is one of the most important questions of the research keeping in mind the prospects of practical application of these new substances and materials on their basis. Therefore, a search of the laws governing the structure of stable (produced, allocated and characterized) fullerenes becomes an actual problem and it may lead to a more successful expanding of their production.

C_{60} (I_h) and C_{70} (D_{5h}) are well-known to be the most stable of all produced fullerenes. Here we shall consider stability of proper (or «empty» higher fullerenes. There are 51 fullerenes which obey isolated pentagon rule (IPR) beginning with C_{60} and up to and including C_{84} . However, only seventeen of "empty" fullerenes have been extracted and identified by now, even though there are much more fullerenes in this rowing that having the closed shell? There are two principal reasons for instability of fullerenes: first one is connected with an open-shell fullerene molecule i.e. its radical nature; and the second one is due to a molecular strain caused by its topology when molecule has a closed shell. In the first case, the radical-containing fullerene may become stable as an endohedral metallofullerene [1].

The quantum-chemical calculations play an important role in investigation of electronic structure and stability of fullerenes. The relative positioning of the pentagons which set the surface curvature of fullerene molecule, presence of condensed hexagons, electronic effects – all of these factors define a total energy of a fullerene molecule and its stability or instability. The analysis has shown that the most stable fullerenes have minimal total energies among their isomers. Nevertheless, the reasons of why some fullerenes can be obtained and others cannot are not clear yet.

2. Results and Discussion

In order to answer these questions we have carried out the analysis of total energies and standard enthalpies of formation of fullerenes per one carbon atom based on the published [2-4] and our own data. Every point of a plot for all stable fullerenes has been connected to the point of C_{60} fullerene. As a result, the allocated sector or "beam of stability" was formed (Fig. 1). Its top border line is defined by the lowest energies and standard enthalpies of formation of fullerenes, whereas the bottom curve defines the border of the highest values of energy and standard enthalpy of formation for all known stable isomers of fullerenes C_N .

The first thing that attracts attention is a stable tendency to energy decrease with an increase of the number of atoms and therefore the size of a fullerene cage (Fig. 1). It is obvious that it reflects the overall decrease of a molecular strain of spheroid molecules going from C_{60} to higher fullerenes.

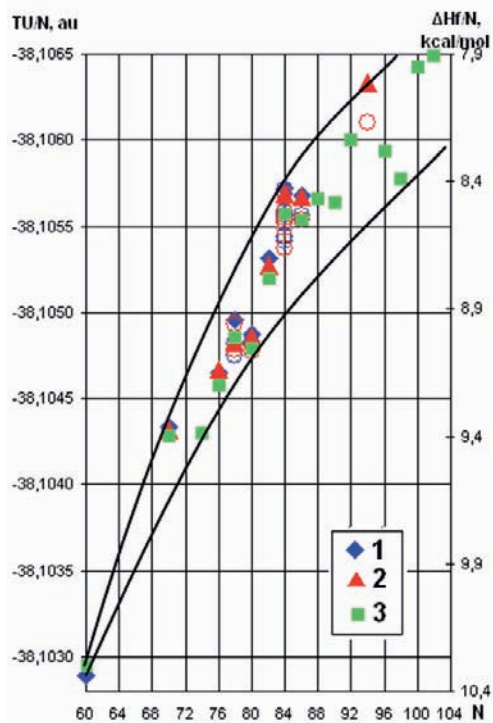


Figure 1. Total energies (TU/N) (1 [2], 2 [our results]) and standard enthalpies of formation ($\Delta H_f/N$) (3 [3,4]) per one carbon of the most stable fullerenes C_N (obtained, extracted and characterized isomers are indicated by a circle).

When the most energetically favorable isomer of the fullerene is located close to a top curve of the beam, it means that there is a possibility of obtaining other isomers which total energy (or enthalpy of formation) lies in a gap defined by a distance from the top to the bottom points of a beam for this fullerene. For fullerene C_{84} this gap can reach 25 kcal/mol. In fact, there are ten extracted and characterized isomers of C_{84} now (a difference in energy reaches up to 20

kcal/mol). And we predict that it is possible to obtain some extra isomers of this fullerene. In contrast, only two isomers of fullerene C_{80} have been extracted. Their energy difference is not higher than 5 kcal/mol, but their calculated energies lay near a bottom border of a beam, which makes it impossible to extract other closed-shell isomers of C_{80} .

It is obvious, that in spite of its prognostic value the discussed procedure is based on integrated parameters of molecular structure and does not allow for judging the reason of stability of one isomer or instability of another. The attempts to work out some criteria of stability (J. Aihara et al.) have failed, because of the absence of analysis of local stability, i.e. the stability of substructures combination of which makes a fullerene molecule. In our opinion the synthesis of fullerenes proceeds by the way of selection of stable substructures. However, as a rule theoretical calculations consider molecule as a whole that seems to be a lack of existing approach of studying stability of fullerenes.

To overcome this problem we have carried out an analysis of π -bonds distribution for the whole number of fullerenes starting from C_{60} and up to C_{84} according to the approach developed earlier [5]. It allowed us to identify a number of fullerene substructures that have electronic features similar to their well-known aromatic analogues, such as naphthalene, indacene, pyrene, perylene, corannulene, coronene, etc. In general, these substructures keep their electronic state irrespectively of the fullerene they belong to.

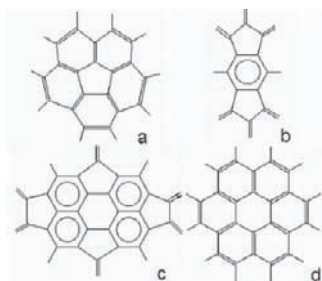


Figure 2. Substructures, mainly characteristic for stable higher fullerenes: corannulene (a), indacene (b), perylene (c), and coronene (d).

It has been found that all of the reviewed stable fullerenes include corannulene (Fig. 2, a) and indacene (Fig. 2, b) - substructures typical for the most stable fullerenes C_{60} and C_{70} . There are perylene (Fig. 2, c) and coronene (Fig. 2, d) substructures present in a structure of some higher fullerenes. The presence of three or more coronene substructures essentially destabilizes the higher fullerene molecules. Anyway, the more the size of a fullerene cage, the weaker this effect that compensates by increasing of fullerene sphere dimension. The analysis of electronic structure of stable (isolated) fullerenes also show that all stable fullerenes have a closed shell and their molecules are characterized by a rather uniform distribution of pentagons along a fullerene sphere.

For example we shall consider a fullerene C_{84} . According to the isolated pentagon rule (IPR), fullerene C_{84} has twenty four possible isomers [6]. Only ten of them (D_2 , D_{2d} , D_{6h} , D_{3d} , D_{2d} , D_2 , C_2 , C_2 , C_s and C_s) have been isolated [2, 7]. However only eight (4 (D_{2d}), 5 (D_2), 11 (C_2), 16 (C_s), 19 (D_{3d}), 22 (D_2), 23 (D_{2d}), 24 (D_{6h})) have been identified. The results of the calculations [2-4, 7,] show that

isomers 11, 16, 19, 22, 23 and 24 are the most stable isomers. At the same time, the energies of two other produced isomers 4 and 5 are comparable, for example, to the energy of isomer 15 (C_s). Apparently, this isomer is not an identified produced isomer with C_s symmetry. The remaining unidentified isomer with C_2 symmetry is, possibly, an isomer 13 (C_2), being the most stable isomer with required symmetry and with the closed electronic shell.

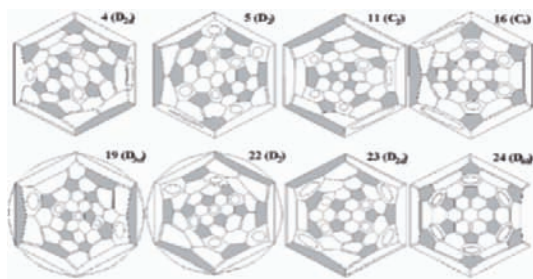


Figure 3. Structure of eight identified isomers of fullerene C_{84} .

The analysis of pi-bonds distribution of eight identified isomers has shown (Fig. 3) that in isomers 4, 5, 11, 19, and 22 only corannulene (Fig. 2, a) and indacene (Fig. 2, b) substructures are present, only indacene (Fig. 2, b) substructure is possible to mark in isomer 23, and the one coronene (Fig. 2, d) in isomer 16 and the two coronene (Fig. 2, d) substructure in isomer 24 appear. This confirms our previous thesis about stabilization of coronene substructures with increase of the fullerene sizes.

3. Conclusion

The analysis of electronic structure of stable (extracted) higher fullerenes has allowed us to reveal the general rules governing their molecular structure. All stable fullerenes have the closed shell and their molecules are characterized by rather uniform pentagons distribution on a fullerene sphere. It is shown, that the opportunity of production of isomers of the higher fullerenes is defined by a position of the most energetically favorable isomer on an offered "beam of stability", that have been constructed according to calculated and experimental data for stable fullerenes, having closed electronic shell.

Acknowledgements

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INVESTIGATION OF THE HYDROGEN INTERACTION WITH $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ BY CALORIMETRIC METHOD

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Abstract. The interaction of hydrogen with nonstoichiometric $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ Laves phase compound at pressure up to 60 atm and in temperature range from 150 to 190°C has been studied by means of calorimetric and P-X isotherm methods. The obtained results allow us to propose the existence of one hydride phase, β -hydride, in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ - H_2 system in the temperature range 150-170°C. It has been found that temperature 190°C is close to critical temperature (182°C) above which hydride phases does not exist.

Keywords: Intermetallic Compounds (IMC); Hydrides; Calorimetry; $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ - H_2 system

1. Introduction

This work is a continuation of our earlier study [1] of the hydrogen interaction with intermetallic compound (IMC) AB_2 -type $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$. The measurements were carried out in twin-cell differential heat-conducting Tian-Calvet type calorimeter connected with the apparatus for gas dose feeding, that permitted us to measure the dependencies of differential molar enthalpy of desorption (ΔH_{des}) and equilibrium hydrogen pressure (P) on hydrogen concentration x ($x=[\text{H}]/[\text{AB}_2]$) at different temperatures simultaneously. The measurements were carried out at 150°C, 170°C and 190°C and hydrogen pressure up to 60 atm.

As mentioned above the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ is a nonstoichiometric compound so, as a matter of fact, it should be correctly written as $(\text{Ti}_{0.89}\text{Zr}_{0.11})(\text{Mn}_{1.39}\text{V}_{0.54}\text{Ti}_{0.07})$ if we want to present it as AB_2 -type. From this record it is clear that Zr and Ti atoms occupy A positions, and Mn, V and over-stoichiometric Ti atoms are distributed in the B positions.

2. Experimental

$\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ was prepared by direct arc melting under purified argon atmosphere of the pure components in stoichiometric proportions. The purity of starting materials was more 99.99%. Since manganese is more volatile than other starting materials a 4% excess of Mn above the intended composition was added to compensate for weight loss during melting. The compound is made homogeneous by several remeltings and is annealed at 1100-1150°C for 240 hours in the sealed quartz ampoule under residual argon pressure 0.01 atm. After annealing procedure the compound was slowly cooled to room temperature at a rate of 0.5°/min. The compound was checked by X-ray, electron microscopy and electron probe analysis.

X-ray powder diffraction revealed that the crystal structure of the sample was characterized as hexagonal C 14-type Laves phase and no second phase was found. The lattice parameters were $a=4.92\text{\AA}$ and $c=8.07\text{\AA}$.

Twin-cell differential heat-conducting calorimeter of Tian-Calvet type connected to the apparatus for gas dos feeding was applied to measure the dependences of differential molar enthalpy of desorption ($\Delta H_{\text{des.}}$) and equilibrium hydrogen pressure on hydrogen concentration in $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}$ and reaction temperature. Hydrogen was obtained by desorption from LaNi_5 -hydride. The apparatus scheme was described elsewhere [2]. The hydrogen concentration in the sample was calculated using the Van-der-Waals equation for pressure below 20 atm and using the modified Van-der-Waals equation for pressure above 20 atm [3]. For stepwise desorption, the initial compositions were: at 150°C $x=2.08$ for $P_{\text{H}_2}=54.0$ atm, at 170°C $x=1.76$ for $P_{\text{H}_2}=54.5$ atm and at 190°C $x=1.46$ for $P_{\text{H}_2}=56.5$ atm.

3. Results and Discussion

The $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}\text{-H}_2$ system has been studied at 150, 170 and 190°C and hydrogen pressure up to 60 atm. Fig. 1 presents the dependences of equilibrium hydrogen pressure (P) versus hydrogen concentration (x) in the intermetallic compound.

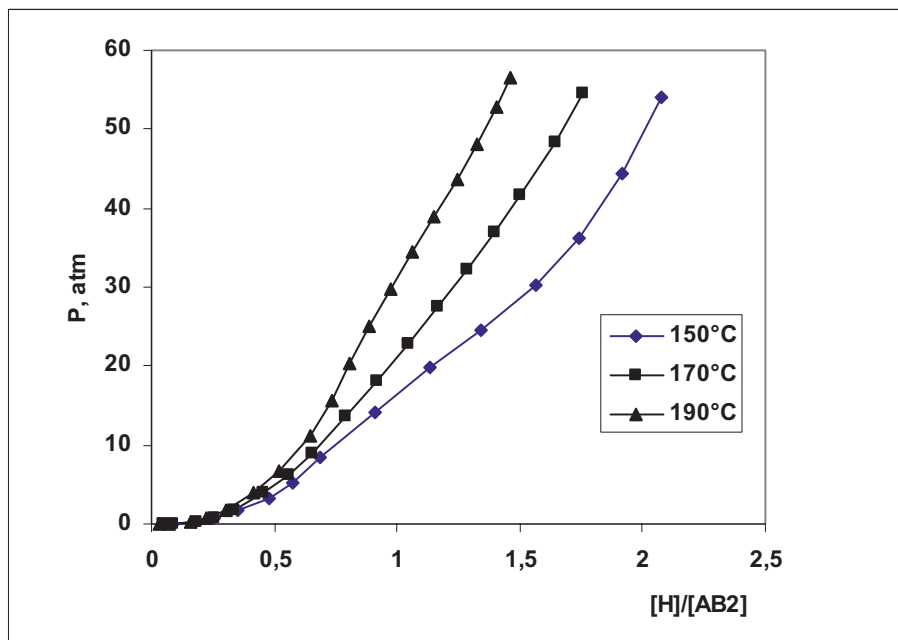


Figure 1. Desorption isotherms for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}\text{-H}_2$ system.

As one can see from Fig. 1 the series of desorption isotherms show a narrowing of the co-existence range with increasing temperature, the plateau slopping increases and at 190°C the plateau region practically disappeared. It should be marked one interesting peculiarity characteristic of obtained isotherms, namely, for everyone the discontinuity in the plateau region when dP/dx reaches a maximum values. The location of this point moves towards smaller values of x with rising temperature, for instance, for 150°C $x \sim 1.04$, for 170°C $x \sim 0.96$ and for 190°C $x \sim 0.80$. The similar tendency in the behaviour of measured P - x isotherms was observed in the previous work [1]. Then the discontinuity in the plot of P vs. x took place at $1.0 < x < 1.2$ and in the temperature range from 81°C to 140°C.

The discontinuity in the plateau slopping was found in the works [4, 5]. Flanagan and co-workers [4] studied the $Ti_{0.8}Zr_{0.2}Fe_{0.1}Mn_{1.5}V_{0.4}-H_2$ system by calorimetric method and established that at $x \sim 1.5$ the plot of function $P=f(x)$ changes its slopping. Sirotina and co-workers [5] researched the $Zr_{0.8}Ti_{0.2}CrFe-H_2$ system and also marked the existence of discontinuity on the plot P vs. x .

Mathematical estimation of a dependence P vs. x carried out for obtained isotherms at 150, 170 and 190°C revealed that the P - x isotherm at 150°C could be described by two second order equations: for $0 < x < 1$

$$P = 19.507x^2 - 2.2059x + 0.0738 \quad (1)$$

and for $1 < x < 2$

$$P = 24.267x^2 - 43.318x + 37.92. \quad (2)$$

Analogous estimations were carried out for 170°C and 190°C and it appeared that the plots of P - x isotherms for two higher temperatures at $x < 1.0$ also were described by second order equations, but at $x > 1.0$ these equations had linear function (see Table 1).

TABLE 1 Coefficients for an equation $P=ax^2+bx+c$.

$t, ^\circ C$	x	a	b	c	$R^2, *$
150	0 – 1.0	19.507	-2.2059	0.0738	0.9981
	1.0 – 2.0	24.267	-43.318	37.92	0.9978
170	0 – 1.0	22.169	-0.643	-0.2076	0.9984
	1.0 – 2.0	0	45.53	-26.243	0.9977
190	0 – 0.8	42.156	-10.059	0.6506	0.9977
	0.8 – 1.5	0	53.498	-22.466	0.9989

* R^2 – squared value on chart

Figure 2 presents the dependence of $|\Delta H_{des.}|=f(x)$ at 150°C. This plot could be divided into three segments: the region of α -solid solution hydrogen in IMC, $0 < x < 0.35$, the $|\Delta H_{des.}|$ values decrease from 41.93 kJ/molH₂ at $x=0.045$ to 30 kJ/molH₂ at $x=0.27$. Further there is a segment with constant enthalpy values, $0.35 < x < 1.25$ ($|\Delta H_{des.}|=28.89$ kJ/molH₂). This region corresponds with $\alpha \leftrightarrow \beta$

transition or plateau region. And, at last, the third segment is a boundary $\alpha+\beta/\beta$ ($1.25 < x < 2.00$). Here the $|\Delta H_{des.}|$ values gradually increase, pass through maximum (38.71 kJ/molH_2 at $x=1.56$) and also gradually decrease, this region corresponds to hydrogen solution in formed β -hydride.

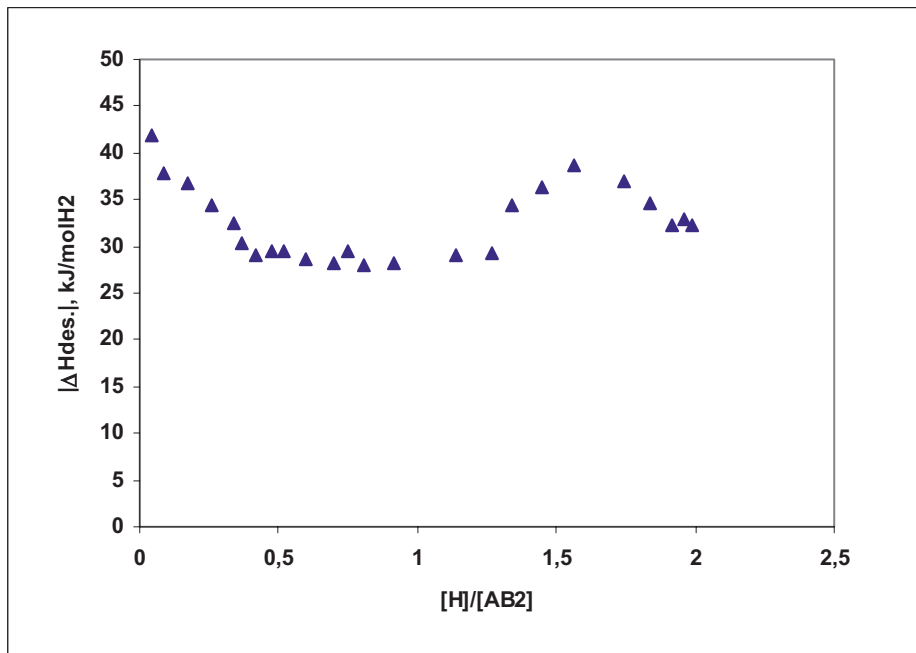


Figure 2. Desorption enthalpy vs. composition at 150°C .

If the dependence of $|\Delta H_{des.}|=f(x)$ obtained at 150°C is compared with the data obtained in earlier work [1] it could be noticed that this dependence drastically changes when experimental temperature increases, namely, at 150°C in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system one region of constant values of differential molar enthalpy exists, whereas at temperatures from 63°C to 140°C there were two regions of constant values of differential molar enthalpies and the existence of two hydride phases, β - and γ -hydride, in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system is proposed.. As well it should be marked that the length of $\alpha \leftrightarrow \beta$ transition at 150°C is significantly larger than those at temperatures from 63 to 140°C (at 150°C the region of $\alpha \leftrightarrow \beta$ transition is $0.35 < x < 1.25$ v.s. at 140°C this one $0.3 < x < 0.9$).

In reference [1] it is suggested, that the formation of β -hydride corresponds the occupation of positions $24(l)$ by hydrogen atoms, and the formation of γ -hydride is connected with the hydrogen occupation of positions $12(k)_1$ and $6(h)_1$. On the base of the data obtained in this work it could be concluded that temperature rising leads to leveling of hydrogen interaction energy with interstitial sites $24(l)$, $12(k)_1$ and $6(h)_1$ that results in the existence of only one hydride.

Figure 3 shows an isotherm of $|\Delta H_{des.}|=x$ for 170°C . From comparison of two dependences presented in Fig. 2 and 3 it is clear that the length of the α -solid

solution region increases when experiment temperature rises from 150°C to 170°C. This region lengthens from 0 up to 0.45 x and the $|\Delta H_{des.}|$ values decreases from 38.32 kJ/molH₂ ($x=0.067$) to 28.46 kJ/molH₂ ($x=0.33$). Further one can see the region of two phases coexistence or the $\alpha \leftrightarrow \beta$ transition region ($0.45 < x < 1.04$), where the enthalpy values remained constant (27.30 kJ/molH₂) and then there is a third segment of the isotherm, $1.1 < x < 1.5$, here again the values of $|\Delta H_{des.}|$ as in Fig. 2 gradually increase, reach a maximum (34.9 kJ/molH₂ at $x=1.28$) and decrease.

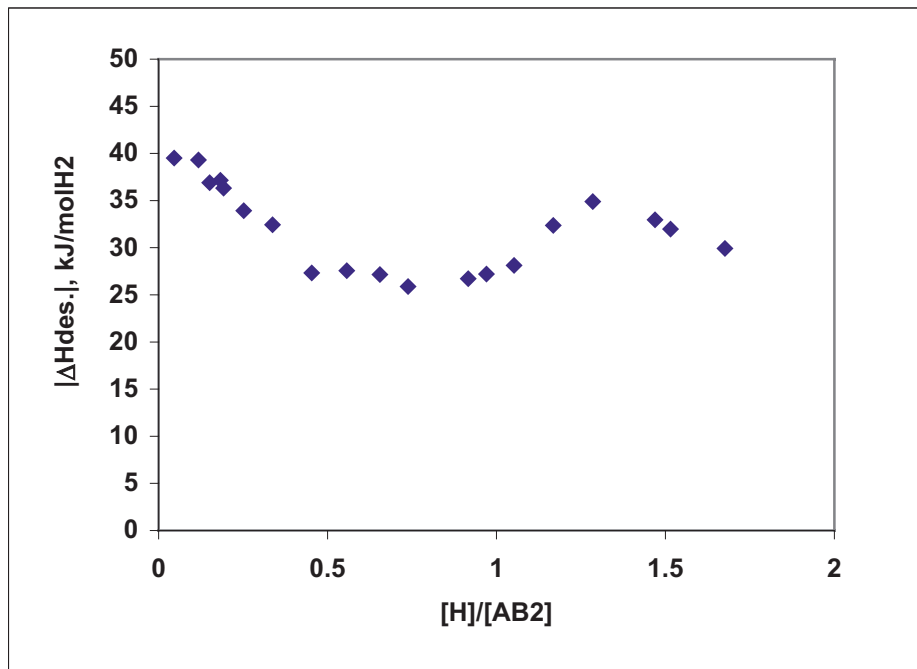


Figure 3. Desorption enthalpy vs. composition at 170°C.

Comparing the enthalpy values of desorption, obtained at 150 and 170°C (see Table 2), it could be marked a small reduction of $|\Delta H_{des.}|$ with rising temperature and at a time the length plateau region shortens. Besides that the large enough length of a boundary $\alpha + \beta / \beta$ ($\sim 0.6x$ for 150°C and $\sim 0.4x$ for 170°C) should be noticed. Such character of $\alpha + \beta / \beta$ transition previously has been marked in reference [4] for Ti_{0.8}Zr_{0.2}Fe_{0.1}Mn_{1.5}V_{0.4}-H₂ system which belongs to the same structure type C14 as the system studied in this work. Flanagan [4] explained such behaviour of Ti_{0.8}Zr_{0.2}Fe_{0.1}Mn_{1.5}V_{0.4}-H₂ system that there is a discontinuity in the enthalpies at the boundary, although the data indicate a smooth transition. The author believed that when increments of H₂ are added or removed in the boundary region this leads to some overlap in enthalpy values, e.g. when a dose of H₂ is added or removed near the end of the plateau, the measured enthalpy may contain contributions from both the plateau and the single phase region because some H₂ will be added to both region.

TABLE 2 Temperature dependence of differential molar enthalpy for the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5} - \text{H}_2$ system

Temperature, t°C	Range	$ \Delta H_{\text{des}} \pm \delta$, kJ/molH ₂
150	$0.35 < x < 1.25$	28.89 ± 0.64
170	$0.45 < x < 1.04$	27.30 ± 0.71

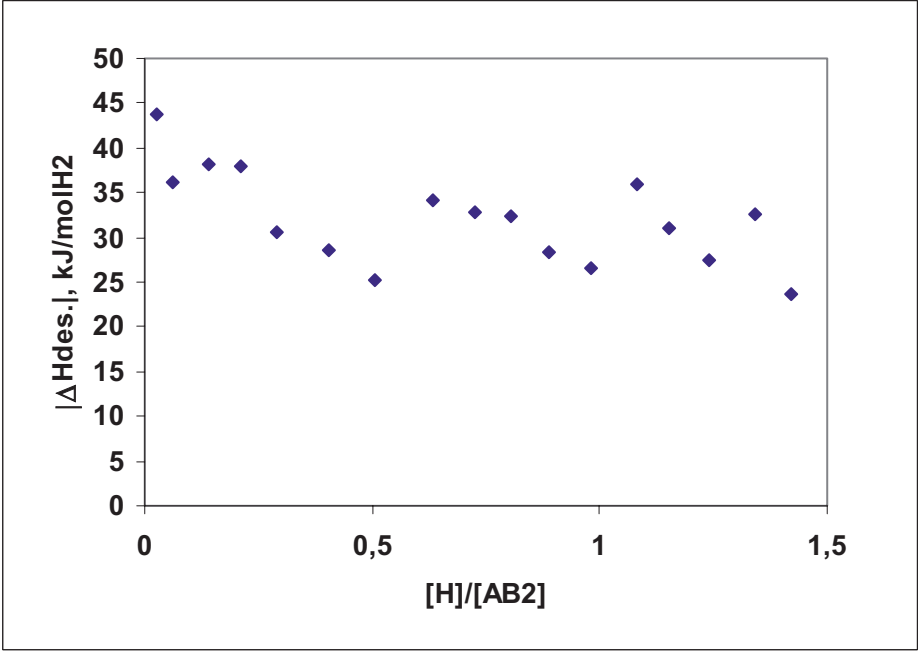


Figure 4. Desorption enthalpy vs. composition at 190°C.

In the plot of $|\Delta H_{\text{des}}|$ - x obtained at 190°C one can define clearly the region of α -solid solution H_2 in the IMC ($0 < x < 0.5$). Within this region $|\Delta H_{\text{des}}|$ decreases from 44.0 kJ/molH₂ ($x=0.25$) to 25 kJ/molH₂ ($x=0.5$). Further the plot of $|\Delta H_{\text{des}}|$ - x can be subdivided into three segments: $0.6 < x < 0.95$, $1.01 < x < 1.25$ and $1.33 < x < 1.60$, where $|\Delta H_{\text{des}}|$ gradually decrease from 35 kJ/molH₂ (at a smaller value of x) to 25 kJ/molH₂ (at a larger value of x) (see Fig. 4). We suppose that such behaviour of a function $|\Delta H_{\text{des}}| = f(x)$ may be connected to the fact that temperature 190°C is closed to the critical temperature (T_c) for this system.

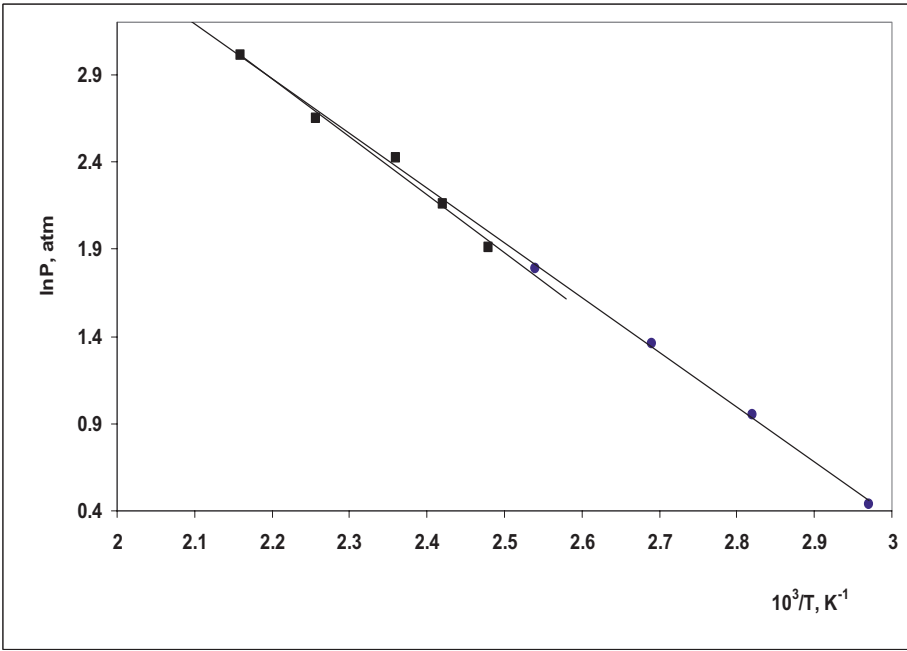


Figure 5. The temperature dependence ln P for the Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.5} – H₂ system at x=0.8.

Figure 5 shows the plot of dependence $\ln P=f(1/T)$ at $x=0.8$. The data necessary for this plot were taken from P-x isotherms, measured within temperature range from 63 to 190°C. It is seen that this dependence is described better by two liner equations

$$\ln P = A/T + B \tag{3}$$

A, B coefficients are presented in Table 3.

TABLE 3. Coefficients A and B for an equation $\ln P = A/T + B$ at $x=0.8$

T, K	-A	B	R ² , *
336-393	3.1454	9.8014	0.9984
403-463	3.3285	10.204	0.9878

* R²–squared value on chart

In our opinion the coordinates of this point of intersection could be regarded at a short run as critical values of pressure and temperature for β -hydride in the Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.5}-H₂ system (P_c=17atm, T_c=455K or 182°C). Above these pressure and temperature in the Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.5}-H₂ system solution (or solutions) should exist in the metallic matrix.

4. Conclusions

Summarizing the data obtained in reference [1] and in this work from reaction calorimetry and equilibrium pressure measurements within temperature range from 63 to 190°C it could be concluded that in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}\text{-H}_2$ system there are two hydride phases, β - and γ -hydrides, within temperature range 63 - 140°C. It was found that further temperature rising to 150°C and 170°C results in a γ -hydride disappeared and one β -hydride exists. On the base of carried out experiments a conclusion that the boundaries of hydride phases and the values of partial molar enthalpies depend on temperature could be made. It was established that temperature 182°C is closed to critical temperature for β -hydride in the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.5}\text{-H}_2$ system above which only solid solution (or some solutions) exists.

Acknowledgements

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INVESTIGATION OF THE PHYSICAL PROPERTIES OF MATERIALS FOR FUEL ELEMENTS AND WORK UP OF LIMIT STATE CRITERIA FOR HYDROGEN CONTAINING SOLID MATERIALS WITH ACOUSTIC MICROSCOPE DEFECTOSCOPY METHODS

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Abstract. In present work we propose the results of acoustomicroscopy investigation the physical properties of materials for fuel elements. In addition, we demonstrate that exposed structure of materials, observe its subsurface layers and determine level of elastic-mechanical characteristics are easy tasks with acoustic microscope defectoscopy methods. Experimental results confirm, that propose methods are effectively for exposing microdefects with different nature. $V(Z)$ -curves methods gives us a possibility to research a nanopore density and to determine the criteria of limit state for hydrogen containing solid materials.

Keywords: method of visualization, acoustic microscopy, subsurface layers, nanopore density, elastic-mechanical steel parameters, nondestructive evaluation.

1. Introduction

The problem of nondestructive express control of physic-mechanical properties of materials in condense state is at present one of the most important scientific problems. Objects of investigations of the most interest were materials, used in processing of fuel elements, and carbon nanostructural materials. In this paper the results of experimental work with the help of acoustic waves gigahertz range are given. The essence of the subjected methods is first inlayer visualization of subsurface structures of the objects under investigation and second in the definition of velocity values of acoustic waves and calculate the elasticity constant of solid material. The nondestructive methods of investigation of structure and characteristics used have not limits by the nature of materials – the objects may be dielectrics, metals, crystals, and other substances, including nanostructural materials. Metals have been chosen as model objects for experimental investigation. Chemical and phase composition, structural, thermo- and deformation properties influence the characteristic properties of the named substances.

The problem of reveals the limit state of solid materials including the hydrogenous ones has become urgent recently. The state of the material when it is close to the loss of stability is called limit. Different limit criteria are applied depending on the operation conditions (force of the temperature, stress, etc.). They

are often different characteristics of physical – mechanical properties. Therefore, the state is limit on the reaching which the material inevitably changes its properties on engaging some structural parameter. It is necessary to reveal such states at the possibly initial stages. First the local structure changes inner stress, physical-mechanical parameters (e.g. the velocity of acoustic waves (AW)) can be used as the limit criteria.

The paper deals with the study of process modifications of the elastic-mechanical characteristics of materials, the damage accumulation, the output of the limit state criteria for them.

2. Experimental

By means of method of visualization with the help of acoustic waves [1,2] we could get the microstructure images of steel samples on different depths from the surface. The analysis of acoustic images gave the possibility to calculate the dimensions of grains, to observe their transformation in the period of time or under external influences. In accordance with the theory of Hall – Peach there were defined the strength characteristics, for example flow limit ($\sigma_{0,2}$) of the materials under study. The significance obtained $\sigma_{0,2}$ is in proper correspondence with values that are table one for the type of steel under consideration.

Example of the obtained acoustic microscope image is represented on Fig. 1. It demonstrated with $\sim 220\times$ magnification, the structure of steel BHC-2M.

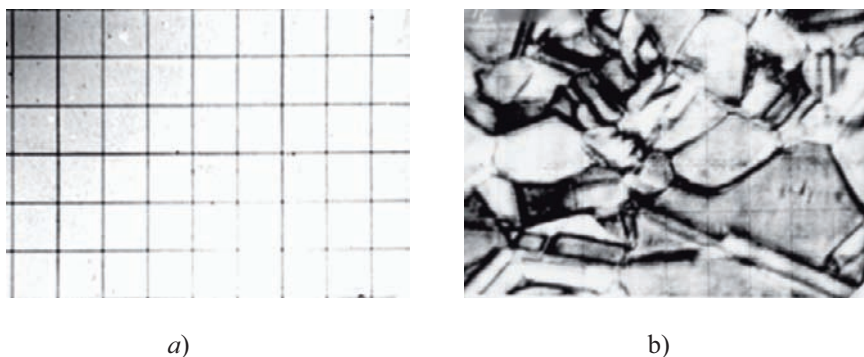


Figure 1. Comparable optical (a) and acoustical (b) images of subsurface layers BHC-2M steel (a) $\sim 200\times$; b) H_2O , $f = 407$ MHz, scale: $28\text{ }\mu\text{m/div.}$, $Z = -12\text{ }\mu\text{m}$).

The comparative optical photo with the same magnification gives the image of a polished surface without revealing structure elements. Structure transformation has been observed after deformational and thermal influences. Acoustomicroscope method of $V(Z)$ – curves essentially increases possibility of obtaining information about investigated materials [3]. It allows to get the specific curves, for given materials, which are connected with elastic – mechanical constant ones. The example of such dependence for carbonaceous steel is demonstrated in Fig. 2.

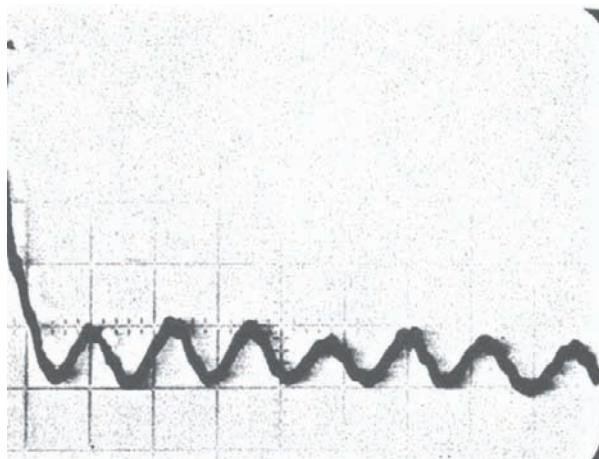


Figure 2. V(Z)-curve for carbonaceous steel (H₂O, vertical scale: 1,0 V/div., horizontal scale: 10 μm/div.).

According to the principles, introduced before [4], the curve received permits to determine the value of SAW velocity. For this it is necessary to measure the distance (ΔZ_N) between maximums, situated on the right of the main one. If the value of acoustic wave velocity v_l in the immersion liquid and the working frequency f are known, then by means of definite experimental interval SAW velocity v_R can be calculated:

$$v_R = v_l \left[1 - \left(1 - \frac{v_l}{2 \cdot f \cdot \Delta Z_N} \right)^2 \right]^{-1/2}.$$

In order to calculate the value of the elastic modules in the local area of the studied material one should use the tabular values ρ_s of density and of Poisson coefficient (ν), or their quantity, determined by one of the certain standard methods:

$$E = v_R^2 \cdot \frac{2 \cdot \rho_s \cdot (1 + \nu)^3}{(0,87 + 1,12 \cdot \nu)^2}$$

and

$$G = v_R^2 \cdot \rho_s \cdot \left(\frac{1 + \nu}{0,87 + 1,12 \nu} \right)^2.$$

There have been developed the acoustomicroscopy methods which allow to extract not only certain values of physical-mechanical properties of materials, but also their correlation dependence on time, schedules of thermal and mechanical processing etc. The examples of the received dependence of arising flocks amount, of speed change of SAW characteristics of fading ($\Delta V/V$), and sizes of appearing heterogeneity on concentration of diffusion hydrogen, appropriate for a number of steels, approve of the thesis above [5]. Adding to it, V(Z) – method makes it

possible to distinguish the characteristics of steels with different deformation degree or with textures. A typical example of revealing such differences is depicted in Fig. 3.

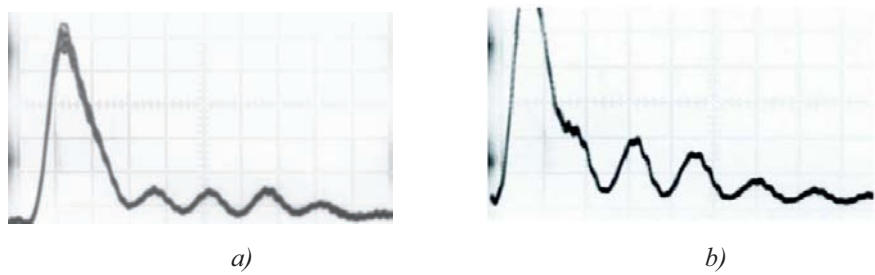


Figure 3. Evaluation of elastic-mechanical steel parameters with different deformation degrees using the methods V(Z)-curves (H₂O, vertically: 1V/div., a) 5% deformation; section is parallel to the plane of rolling; horizontal scale: 10,6 μm/div., ΔZ_N = 13,74 μm, v_R = 2,98·10³ m/s; b) 50% deformation; section is parallel to the plane of rolling; horizontal scale: 12,5 μm/div., ΔZ_N = 14,95 μm, v_R = 3,11·10³ m/s)).

Finally, let us move to the investigating of the physical properties of nanostructural carbon materials. As mentioned already the methods of acoustomicroscope defectoscopy are applicable to almost all materials in condensed state. The opportunity of their usage for carbon materials is demonstrated on the graphite PROG, that is chosen as a model. Its main characteristics, determined with the help of acoustomicroscope methods, are illustrated in the Table 1.

TABLE 1. Main characteristics of the graphite PROG determined by V(Z)-method

Characteristic	Value
SAW velocity, v _R (10 ³ m/s)	2,01
Module of elasticity, E (10 ⁹ Pa)	12,77
Interval, ΔZ _N (10 ⁻⁶ m)	5,6
Poisson coefficient, ν	0,14
Porosity, θ (%)	14
Density, ρ _s (10 ³ kg/m ³)	1,124

The sensitivity of the employed materials towards nanoinhomogeneities, which sizes are much less than the resolvable ability of SAM, deserves an individual examination. The example of a form change in V(Z) – curves for the glass of different nanopore density is presented in Fig. 4.

The limit state reveal at the initial stages can be carried out by sensitive to microinhomogeneous methods. The limit criteria are possible to be evaluated according to the quantity, form, and distribution in volume of such inhomogeneities. Acoustic microscope defectoscopy methods actively developing in the in the latest 15 – 20 years can be referred to such methods [4,5,6]. They

allow both to get subsurface acoustic images of object microstructures and to define their physical – mechanical characteristics. Therefore, it was suggested to apply a scanning acoustic microscope (SAM) of the reflective type [3,7] for the nondestructive control of the hydrogenous materials.

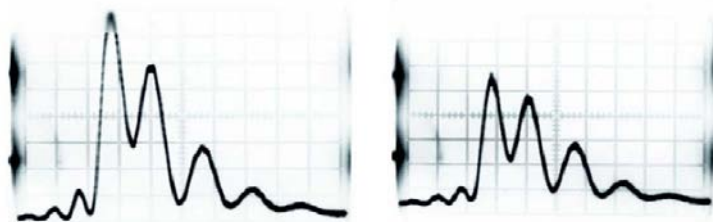


Figure 4. Change $V(Z)$ -curves form in the areas of different nanopore density in the glass trade TPS (H_2O , vertically: 0,25 V/div., horizontal scale: 12 $\mu m/div.$, $\Delta Z_N = 19,37 \mu m$, $v_R = 3,53 \cdot 10^3$ m/s; $(\Delta V/V)_{max} = 41\%$).

In Fig. 5 the acoustic image of subsurface layers of the steel sample (08X21H6M2T), subjected to corrosion is presented. The pitting with the special dimensions of 3 – 15 μm are visualized with high resolution. Besides, the depth of demonstration of the defects, their dimensions and quantity in the raster allow to judge by the limit state. It was not possible to reveal such inhomogeneities both at the optical images and with the help of some other scientific methods. The other example of the output of the limit state criterion is connected with the appearance in the hydrogenous metals of the cracks of flocken type.

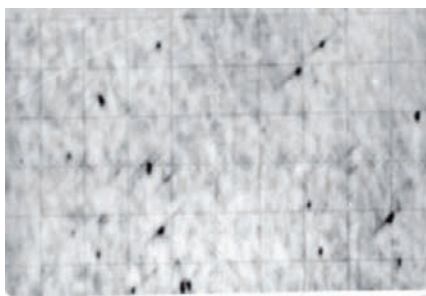


Figure 5. The pitting in steel (scale 35 $\mu m/div.$, Hg, $Z = -7 \mu m$).

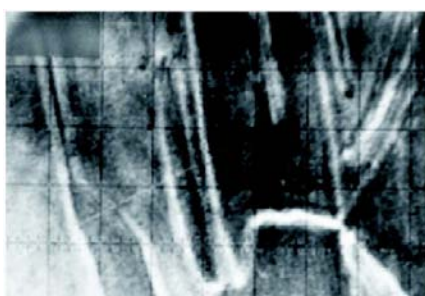


Figure 6. Microcrack in steel (scale 20 $\mu m/div.$, Hg, $Z = -40 \mu m$).

The material reliability is evaluated concerning its dimensions, dynamics of development, increase velocity.

In Fig. 6 the acoustic microscopy image of a microcrack in the austenite class steel at the depth of $\sim 40 \mu m$ is presented. It is also possible to apply acoustic microscopy methods based on the use of $V(Z)$ – curves for the study of the limit state of the materials in a solid state [6-8].

It makes it possible to calculate the values of velocities SAW and to define the quantity of the coefficient changes of AW fading in the material at the relative modification $\Delta V/V$ of height of the main maximum of the $V(Z)$ – curves. The

elastic – mechanical characteristics of material change at the diffusion into hydrogen material, which manifests itself in the changes of velocity SAW v_R and the level of $\Delta V/V$.

The control technology of limit state with appliance of $V(Z)$ – curves consists of the analysis of their form transformation. The values of velocities of surface acoustic waves (SAW) and the change of the level of their fading were calculated due to the special dependencies. The limit state of material conclusion was made according to the dimension of local fluctuations of physical – mechanical parameters. The example of inhomogeneity distribution in the investigated object, with the appliance of the $V(Z)$ – curves is presented in Fig. 7. As a model in this case the glass with microdefects included was used. The number and dimensions of microdefects are one of the criteria of limit state.

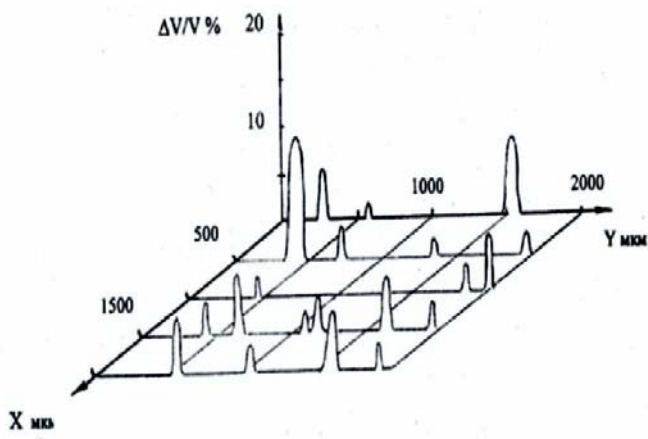


Figure 7. It is an example of the inhomogeneity distribution watch and dimension measure of microdefects in the glass object, inside raster $2 \times 2 \text{ mm}^2$.

It is possible to estimate the value and some other sample characteristics, for example the hydrogen concentration, according to the changes of the velocity SAW and the relative height $\Delta V/V$ of the maximum $V(Z)$ – curve.

The dependencies both between the hydrogen concentration and the number of the microcracks emerged, and the values of velocity SAW on depth of the hydrogen penetration into the sample, period of diffusion, etc. are received at that. The limit hydrogen concentration in this material can be evaluated concerning the value of velocity SAW from the received dependence for steel (Fig. 4).

The results of the experiments illustrating the possibility to define the thickness of the modified layer caused by hydrogen diffusion in the metal materials according to the value of velocity SAW or the ratio $\Delta V/V\%$ were presented before. Difference between initial and modified material according to these characteristics can reach 5–20%.

And, finally, the limit state of material is defined considerably by the parameters of the mechanical influences on it including the number of load cycles. The accumulation of damage defects in the material takes place at the increase of the cycles of influence on the material. The process under consideration can reach the extreme parameter on the intersection of which the investigated object will be

destroyed. It is possible to define this extreme parameter with the appliance of the $V(Z)$ – curves. In Fig. 9 the result of investigations of the dependence of the value of AW absorption level ($\Delta V/V\%$) on the number of load cycles for steel 08X18H10T is presented.

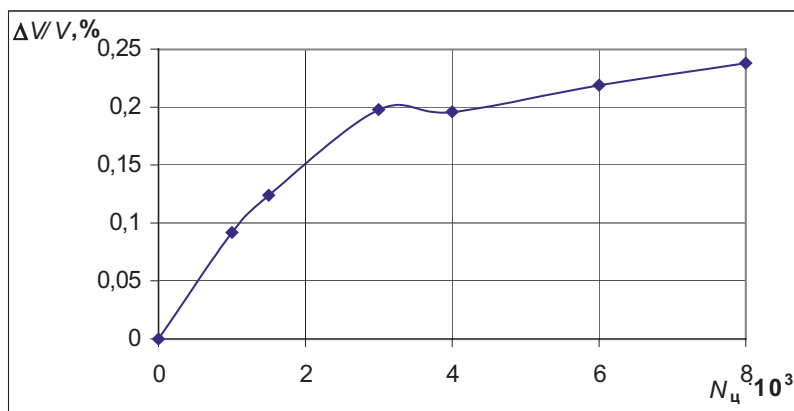


Figure 8. Dependence of velocity SAW in steel 55XH on the hydrogen concentration level.

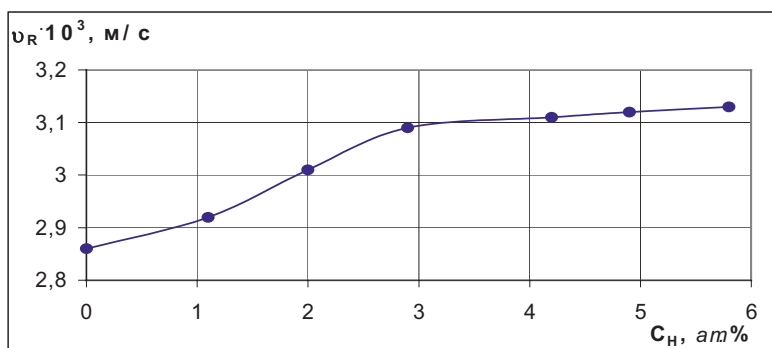


Figure 9. Dependence of the absorption level ($\Delta V/V\%$) on the number (N_u) of load cycles for steel 08X18H10T.

It can be seen from the picture that the sharp, practically line height of the absorption level is observed at the increase of the cycles to 3000. This proves the active flow of the processes of the structure reorganization. The absorption level is not changed up to 8000 – 9000 cycles, then a significant increase resulting in destruction (at 15000–17000 cycles) starts.

3. Conclusions

To sum up, the acoustomicroscope defectoscopy methods are promising in studying the physical characteristics of the materials, employed for fuel elements and for carbon nanostructural materials. The results obtained have proved the

possibility of output of the limit state criteria of the hydrogenous materials by applying acoustic microscope defectoscopy methods.

Acknowledgements

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ELECTROLYTIC PRODUCTION OF CARBON NANO-TUBES IN CHLORIDE-OXIDE MELTS UNDER CARBON DIOXIDE PRESSURE

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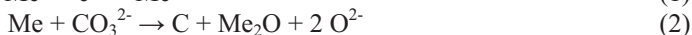
Abstract. The electrochemical study of peculiarities of carbon solid phase electrodeposition from halide melts (NaCl:KCl, mole ratio 1:1; NaCl: KCl:CsCl, mole ratio 0.3: 0.245: 0.455), saturated by carbon dioxide under excessive pressure up to 1.5 Mpa was carried out in temperatures range 500 ÷ 800 °C by the method of cyclic voltammetry. It has been found that the cathodic process occurs in three stages at sweep rates of $\leq 0.1 \text{ Vs}^{-1}$, and its electrochemical-chemical-electrochemical (ECE) mechanism has been suggested. The chemical, phase and structural composition of cathode products were determined. It has been found that cathode deposits contain carbon nano-sized particles of different forms and structure: blocks of amorphous carbon, crystalline graphite, carbon nanotubes (CNT) and nanofibres. The majorities of obtained CNT are multi-wall and have a curved form. Most often CNT are collected in balls, rarely – are located as individual tubes. As a rule, tubes of one diameter organize one ball. Outer diameter of tubes is from 5 to 250 nm, and internal diameter is from 2 to 140 nm. Correlation between product structure and yield against electrolysis conditions and regimes were established.

Keywords: carbon nanoparticles, carbon nanotubes; electrochemical treatment; transmission electron microscopy; particle size.

1. Introduction

The study of carbon electrodeposition from carbonate and halide- carbonate melts was devoted a cycle of works [1 - 6]. It was found that under certain conditions carbon solid phase was formed on cathode with 100 % current yield. The questions of product morphology, structure and dispersity had remained not opened because of absence at that time analysis technical equipment with high-resolution. Different schools of the electrochemists offered various mechanisms of carbon phase formation:

- (1) – electroreduction of alkaline metal ion on the cathode, which further makes chemical reduction of carbonate-anion up to carbon:



- (2) - direct discharge of carbon-anion up to carbon on the cathode



- (3) – realization of previous chemical reaction of the acid-basic type with the subsequent discharge of carbon dioxide up to carbon on the cathode:



According to the last mechanism an electrochemical active particle is carbon dioxide. Therefore direct electroreduction of carbon dioxide, dissolved in the salt melts must also give a carbon as a cathode product. It was confirmed in the [6, 7], but there were no any data about morphology and structure of obtained carbon powders. The electrodeposition of carbon from carbon dioxide was taken as the base process for high-temperature electrochemical synthesis (HTES) of refractory carbides [8, 9].

The aim of the present work is the fulfillment of the complex studying: (a) – investigation of peculiarities of carbon solid phase electrodeposition from halide melts, saturated by carbon dioxide under excessive pressure up to 1.5 MPa in temperatures range 500 - 800 °C; (b) – elucidation of electrode processes mechanism; (c) - characterization of produced carbon powders; (d) – establishment of correlation between product structure and yield against electrolysis conditions and regimes.

2. Experimental

2.1 CHEMICALS AND MATERIALS

The mixtures of extra pure sodium, potassium and cesium chlorides of different compositions were used as the solvent melt. Two electrolytes were employed: a ternary eutectic (NaCl, KCl, CsCl, mole ratio 0.3: 0.245: 0.455 with melting point 480 °C), and binary mixture (NaCl, KCl, mole ratio 1:1 with melting point 660 °C). Each electrolyte was prepared firstly by thermally drying each salt in air at 150 °C during 12 h. and then by pre-melting 60 g of the appropriated mixture in the platinum crucible. The purity of the mixture was checked by residual current magnitude ($i_{\text{res}}=1.2 \text{ mA/sm}^2$ at $E = -1\text{V}$). Carbon dioxide was used from gas-cylinder of trade mark (99.8 % of the main compound) after drying by silica gel, which was in the intermediate gas container (12) in Fig. 1. Platinum, golden wires and glassy carbon cores (diameter: $0.5 \div 1 \text{ mm}$, area of the electrodes: $\sim 0.2 \div 0.5 \text{ sm}^2$) were used as fully- or semi-doped indicator electrodes. Crucibles made from glassy-carbon or platinum served as the counter electrode and melt container at the same time. The potentials were measured versus quasi-reference electrode - platinum wire (diameter - 1 mm, area – 5 cm^2). The peculiarities of electrochemical behavior of this reference electrode in the case of change of the gas phase over the chloride melt was described in [9].

2.2 APPARATUS, MEASUREMENTS AND ANALYSIS

The electrochemical behavior of carbon dioxide under excessive pressure was investigated in a hermetically three-electrode cell made of special stainless steel, which permitted measurements at temperatures up to 900 °C and at an excessive gas pressure up to 2.0 MPa (Fig. 1).

Voltammetry with single and cyclic potential sweep was chosen as the electrochemical method of investigation. $I - E$ curves were obtained with a PI-50-1 potentiostat in a polarization rate range of $0.005 \div 0.1 \text{ V/s}$. Investigations were carried out in a temperature range of $500 \div 850 \text{ °C}$ and at a CO_2 pressure of $0.1 \div 1.5 \text{ MPa}$. The temperature of the melt was maintained with accuracy to $\pm 2 \text{ °C}$. All

experiments were made with first evacuating the system to -1 atm. and then passing carbon dioxide through the system for 10 minutes. After that the needed pressure was produced in the cell. Polarization curves were taken after keeping the system under isothermal and isobaric conditions for no less than 1 h, i.e. after attaining the equilibrium:



The electrolysis of the studied systems was carried out in the same cell as voltammetry measurements under the mode of either constant current or voltage. In the constant current mode, the applied current density was in the range of $0.01 \div 0.2 \text{ A/sm}^2$ with reference to the surface area of the cathode before starting the electrolysis. Semi-immersed glassy carbon plate electrodes (cathode area -5 sm^2 , anode area -10 sm^2) were used while electrolysis experiments. A powder product was either settled down onto the crucible bottom or assembled on the cathode in the view of electrolytic "pear". The deposit was separated from salts by successive leaching with hot water. Thereafter, the precipitate was washed with distilled water by decantation method several times and dried to a constant mass at $100 - 150^\circ\text{C}$. The electrolysis products were analyzed by chemical and X-ray phase analyses, methods of electron diffraction and electronic microscopy (transmission and scanning).

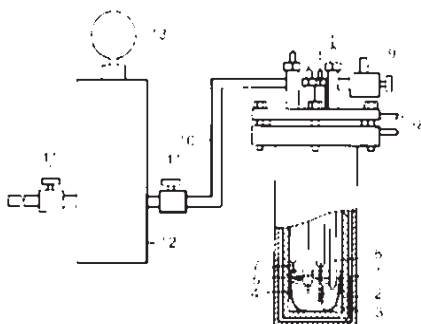


Figure 1. Principal circuit of high temperature cell for voltammetry investigations under excess gas pressure: 1 - high-temperature stainless steel box; 2 - quartz box; 3 - crucible and country electrode; 4 - indicated electrode; 5 - reference electrode; 6 - thermocouple; 7 - Pt lead wire for crucible; 8 - water cooling for cell cover; 9 - valve of pressure release in cell; 10 - hose coupling; 11 - gas control valves; 12 - intermediate gas container (filling volume - 2 liters); 13 - gauge-pressure manometer.

3. Result and Discussion

Voltammetry study made on platinum and gold needle-shaped electrodes have shown, that at low electrode polarization rates ($\leq 0.1 \text{ V}\cdot\text{s}^{-1}$) voltammograms exhibit two well-defined waves of carbon dioxide electroreduction with limiting currents and half-wave potentials - (A) $E_{1/2} = -0.44 \text{ V}$; (B) $E_{1/2} = -0.78 \text{ V}$ (Fig. 2).

On the reverse sweep, no anode current is observed after the first wave. If reversal of the sweep takes place after the limiting current of the second wave, two waves (C) and (D) appear on the reversal sweep on Pt electrode. As the reversal potential shifts towards more negative values, the first - wave (C) current decreases, and the its potential remains unchanged; the peak potential of the second

wave (D) shifts towards more positive values, and its current increases. The differences of $I - E$ – curves obtained on the gold electrode (Fig. 2b) consists in presence only one wave (D) on the reverse sweep of voltammogram, that is presumably connected with absence of carbon alloy-forming with gold. To elucidate the mechanism of the processes occurring on the cathode, the electrolysis's in the constant potential current mode at first-wave and second-wave

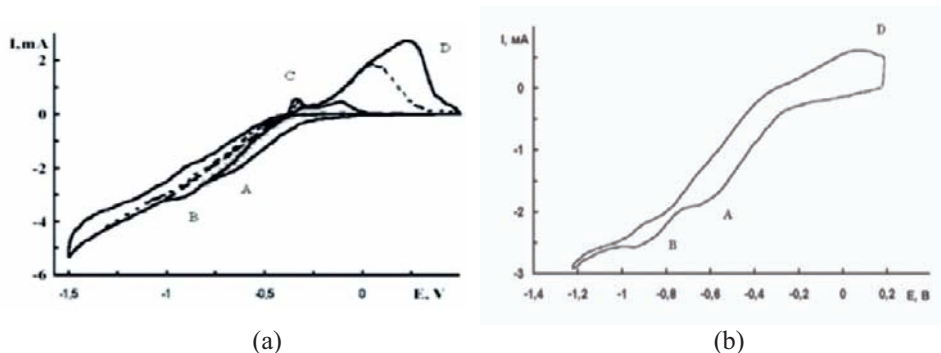
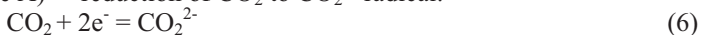


Figure 2. Cyclic voltammograms of NaCl-KCl-CO₂ melt at temperature 750 °C and CO₂ pressure $1.0 \cdot 10^5$ Pa, potential scan rate $-0.1 \text{ V} \cdot \text{s}^{-1}$: (a) - on Pt electrode at various potential reverses; (b) – on golden electrode.

potentials have been carried out. Electrolysis at the first-wave potential gave gray unsound deposits with fairly good adhesion but with low current densities ($i_k \leq 0.005 \text{ A} \cdot \text{cm}^{-2}$). In electrolysis at the second –wave potential, also unsound but black deposits were obtained. In the case of electrolysis in the constant current mode, the adhesion and homogeneity of the film are better than those of films deposited under potentiostatic conditions. The electrolysis's of different duration at several CO₂ pressures and several temperatures (700, 750, 800, 850 °C) were carried out but this had no noticeable effect on the quality of the obtained films. A microprobe analysis of the deposits has been performed; it showed the gray deposits to consist only of electrolyte impurities (Ca, Mg, Si, Zn and some others), which should not have deposited at the given potentials, and the black deposits to consist mainly ($\geq 98\%$) of carbon. Electron-diffraction method while reflection showed it to be polycrystalline graphite (Fig. 3 c).

Based on the analysis of the obtained data the ECE (electrochemical-chemical-electrochemical) mechanism of CO₂ electroreduction can be suggested:

First stage: (wave A) - reduction of CO₂ to CO₂²⁻ radical:



The radical formed is an unstable species, which possesses strong reducing properties and reduces small impurities in the electrolyte.

Second stage: chemical formation of carbon monoxide



Third stage: (wave B) - irreversible electroreduction of CO to elementary carbon



As the same time carbon dioxide acts as acceptor of oxide anions and the summery cathode reaction can be presented as:



Carbonate-ion discharge takes place at anode with producing carbon dioxide and oxygen:



The summary electrodes reaction is:



In order to determine current yield and to study phase and structure composition of carbon cathode product the electrolysis with different current densities ($i_k=10\div 200 \text{ mA/sm}^2$) were carried out in the system KCl - NaCl (1:1) – CO_2 ($P_{\text{CO}_2} = 5\div 10 \text{ atm.}$ and $T = 750^\circ\text{C}$). It was found that structure of carbon cathode deposits depends from melt temperature, carbon dioxide pressure, current densities and contain carbon nano-sized particles of different forms and structure: blocks of amorphous carbon, crystalline graphite, carbon nanotubes (CNT) and nanofibres. The majorities of obtained CNT are multi-wall and have a bent (curved) form. Most often CNT are collected in balls, rarely – are located as individual tube. As a rule, tubes of one diameter organize one ball. Outer diameter of tubes is from 5 to 250 nm, and internal diameter is from 2 to 140 nm. Almost all tubes are filled partly by electrolyte salt. With the increase of current density the tubes diameter is decreased (although every product, obtained in studied current densities has tubes of different diameters). At the same time the carbon product output and the portion of CNT in the general mass of this product are increased. The results of the microscopic researches of obtained carbon products are presented on the Fig. 3.

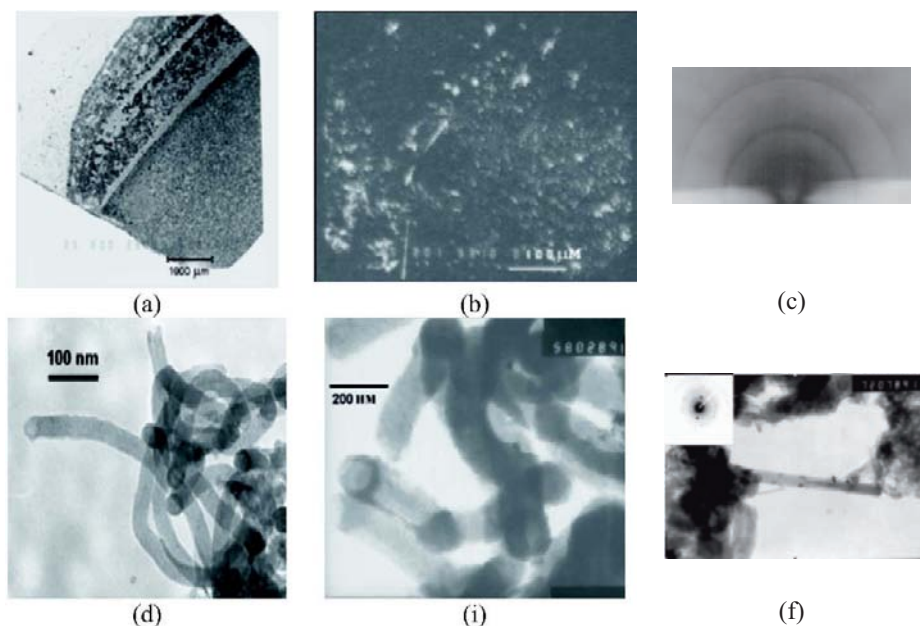
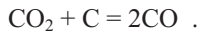


Figure 3. Photomicrographs of cathodic products of the system NaCl-KCl- CO_2 , obtained at different electrolysis conditions: (a) – gray coating ($E_k = -0,6 \text{ V}$, $P_{\text{CO}_2} = 10 \cdot 10^5 \text{ Pa}$; $T = 750^\circ\text{C}$); (b) – black coating and its electron -beam image (c) ($E_k = -1 \text{ V}$, $P_{\text{CO}_2} = 5 \cdot 10^5 \text{ Pa}$; $T = 850^\circ\text{C}$); (d), (e), (f) – fragments of black powders produced at $P_{\text{CO}_2} = 10 \cdot 10^5 \text{ Pa}$; $T = 750^\circ\text{C}$ and $i_k \text{ (mA/sm}^2\text{)} = 13.5; 28; 56$ corresponding.

The maximum current yield of the carbon phase in the melt NaCl – KCl does not exceed 30%, that is connected apparently with cathode product loss due to passing reaction at temperatures above 600 °C:



In order to arise current yield of carbon phase it is advisable to use more low-melting electrolytes. For this purpose the electrolysis of CO₂ in the ternary eutectic Na,K,Cs|Cl at temperature 500 °C was carried out. In this system carbon current yield was arisen up to 80 % and the cathode product contained fullerenes phase (according to X-ray analysis) together with carbon phases obtained in NaCl – KCl melt.

Conclusions

1. Electroreduction of carbon dioxide up to carbon can be taken as the base of high-temperature electrochemical synthesis (HTES) of various nano-sized carboniferous inorganic compounds: carbon films and powders of different structures.
2. The principle possibility of carbon nanotubes generation by the electrolysis of molten salts saturated by carbon dioxide was shown. The method advantage is the apparatus simplicity, ecological cleanness, economy, possibility of control of product structure and morphology by choice of the optimum electrolysis conditions.

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INVESTIGATION OF DELAYED HYDRIDE CRACKING IN THE Zr-2,5% Nb ALLOY

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Abstract. DHC velocity in Zr-2.5%Nb alloy for different hydrogen concentrations were investigated using specimens prepared from the both CANDU and RBMK Zr-2.5%Nb fuel channel pressure tube material. Sections of the pressure tube were hydrided to produce hydrogen concentration up to 72 ppm using an electrolytic method and diffusion annealing treatment. From hydrided pressure tube material compact toughness specimens were made. Axial cracking velocity was determined on fatigue pre-cracked specimens under constant loading and initial K_I value of $15 \text{ MPa}\cdot\text{m}^{1/2}$.

The experiments show that DHC velocities in RBMK TMO-1 samples are 3-5 times lower than in CANDU pressure tube material.

Keywords: zirconium, hydride, delayed hydride cracking

1. Introduction

Zirconium alloys are used as a constructional material for manufacturing of cladding of fuel assemblies and fuel channels of RBMK, as well as CANDU type reactors [1]. Zirconium alloy (Zr+2,5% Nb) absorbs hydrogen during operation as a consequence of the corrosion reaction with water. Hydrogen has very limited solubility in zirconium alloys; when the thermal solid solubility (TSS) [2] is exceeded in a component such as pressure tube that is highly stressed for long periods of time, delayed hydride cracking (DHC) failures may occur. DHC is a phenomenon where a crack can propagate in stepwise fashion as a result of hydrogen redistribution ahead of the crack tip under a stress level below the yield stress. If stress levels are sufficiently high the local hydrogen concentration can exceed the TSS, and the hydride platelets precipitate in the primary cracking direction. When a platelet reaches a critical length, it cannot support the local stress and it ruptures. The crack advances this distance and it arrests in the fracture resistant zirconium matrix. Repetition of this process causes continued cracking. This incremental growth of the crack forms a striation on the fracture surface. There is an incubation period between each crack growth increment while a new hydride zone is formed at the crack tip [3]. DHC has been recognized as the potential cause of failure of pressure tubes in both CANDU [4] and RBMK reactors [5].

2. Experimental

Sections of the pressure tube were hydrided to produce required hydrogen concentration using an electrolytic method and diffusion annealing treatment.

Hydrogen homogeneity was controlled by metallographic examination. Metallography of hydride structure on radial-axial and radial-transverse sections shows a uniform hydride distribution with hydrides elongated in the longitudinal direction (Fig. 1). From the hydrided pressure tube material curved compact toughness (CTT) specimens were machined. Except for the thickness and the curvature of the tube, the in-plane dimensions of specimens were in proportion described for compact specimen in ASTM standard test method (E-399).

The CCT specimens have been fatigue pre-cracked at room temperature to produce an initial crack length about 1.7 mm. Then specimen has been loaded to give K_I values at range of $14 \text{ MPa}\cdot\text{m}^{1/2}$ to $15 \text{ MPa}\cdot\text{m}^{1/2}$. Test ended after estimated crack length has reached about 1.5 mm.

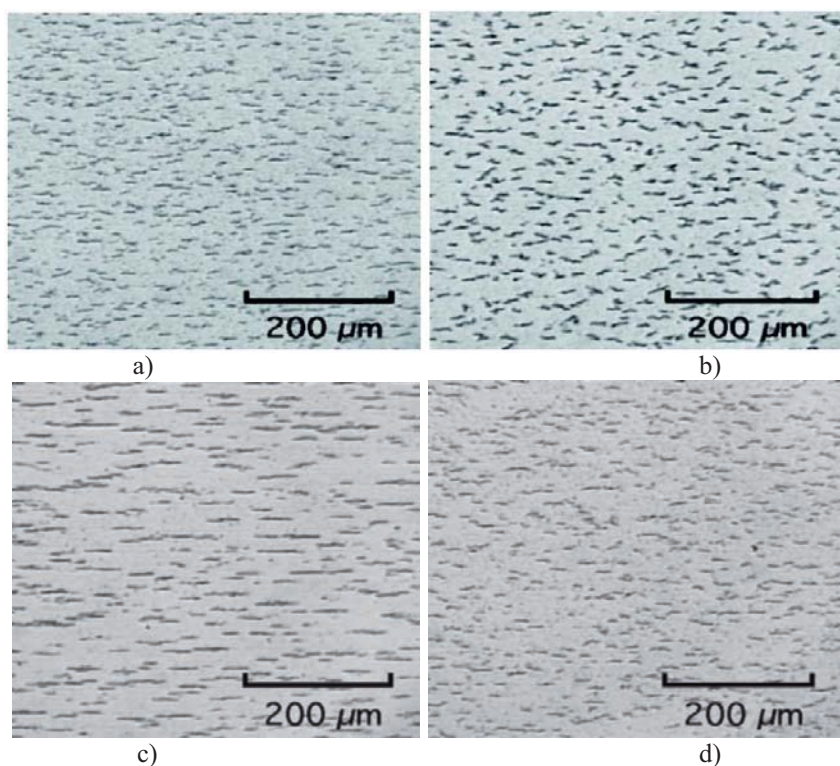


Figure 1. Hydride microstructure of CANDU(a, c) and RBMK (b, d) pressure tube material in radial-transverse (a, b) and radial-axial(c, d) sections. Hydrogen concentration 76-79 ppm.

After completion of DHC test specimen has been unloaded and cooled down in the furnace to the room temperature. Specimen then has been subjected to cyclic loading to outline the DHC crack and then fractured. After completion of DHC test actual crack length was measured from fractographs (Fig. 2).

The average cracking velocity has been determined by dividing average DHC length by cracking time. DHC velocity data as a function of $1000/T$ are plotted in Fig. 3.

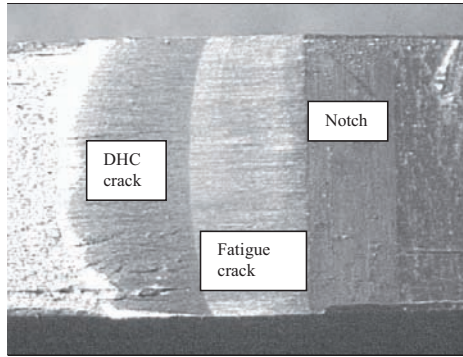


Figure 2. Area method for average DHC length measurement from fractured surface of CCT specimen.

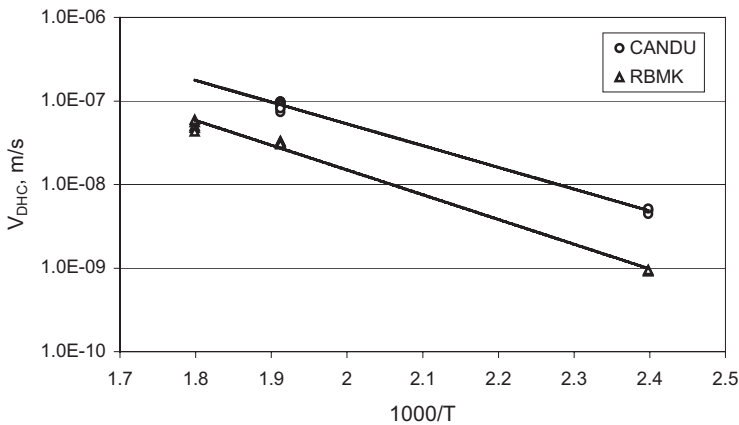


Figure 3. DHC velocity results for CANDU CW and RBMK TMO-1 pressure tube material.

The propagation of a crack creates lines on the fracture surface, which lie parallel to the crack front, perpendicular to the direction of crack growth [6]. Each incremental advance of the crack front results in the formation of a striation on the fracture surface (Fig. 4a). Temperature dependence of inter-striation spacing, measured from the fracture surface of the tested specimens is presented in Fig. 4b.

3. Conclusions

DHC velocities in RBMK TMO-1 samples, depending on temperature are 3-5 times lower than in CANDU pressure tube material. Crack growth in RBMK pressure tube material occurs at larger increments of the crack front. Striation spacing increases with increase in test temperature and appear to be larger in the specimens of the RBMK material than in the CANDU material.

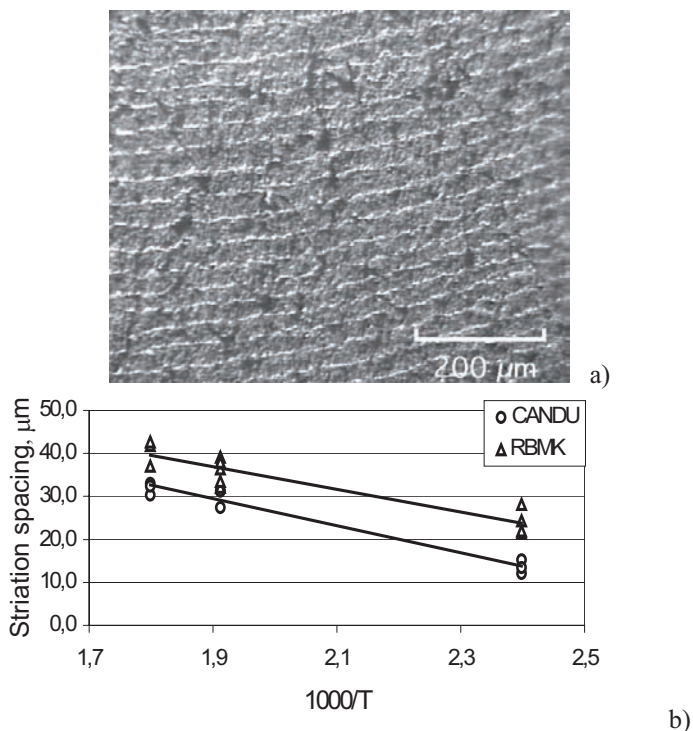


Figure 4. Striations on the DHC fracture surface (a); relationship between inter-striation spacing and temperature (b).

Acknowledgements

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SOLITON LATTICES IN CARBON NANOTUBES

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Abstract. Calculations of the non-linear wave functions of electrons in single wall carbon nanotubes have been carried out by the quantum field theory method namely the second quantization method. Hubbard model of electron states in carbon nanotubes has been used. Based on Heisenberg equation for second quantization operators and the continual approximation the non-linear equations like non-linear Schroedinger equations have been obtained. Runge-Kutt method of the solution of non-linear equations has been used. Numerical results of the equation solutions have been represented as function graphics and phase portraits. The main conclusions and possible applications of non-linear wave functions have been discussed.

Keywords: Carbon nanotubes; Hubbard model; Continual approach; Non-linear equations; Regular solutions; Soliton lattices

1. Introduction

The progress in researches of carbon nanotube forms started with S. Iijima's paper [1] in 1991. Nanotubes represent the hollow cylinders with micro size lengthwise and some nanometers across diameter, which walls include one or few graphite layers consisting of six-member rings (hexagons). The further experimental and theoretical researches have shown that nanotubes are new advanced materials with the unique properties: high solidity, a conductivity (metallic or semi-conductor) and numbers of other properties, which are interesting and important for their future applications, for example, in the field of microelectronic [2 - 4]. The tubes properties depend on their form and curvature of a surface, a way of doping and choice of an introduced element etc. Development of technology dealt with nanotubes leads to creation of new physical objects showing the unique physical-chemical properties. The comparative simplicity of carbon nanotube structures and its quasi-one-dimensionality have made these matters very popular for theoretical and experimental scientists.

Among all specialties of carbon nanotubes the non-linear properties (acoustical or electromagnetic descent) are special interesting last years. In particular, one should to notice that the non-linear properties of nanotubes connecting with inharmonious potential of the interaction between neighboring carbon atoms have been researched using a reduction to Korteweg-de Vries and other non-linear equations in works [5 - 7]. In present paper our attention focuses primarily [8 - 10] on non-linear properties of nanotube concerning of the strong electron interaction.

2. Experimental

We shall consider single walled carbon nanotube (SWNT) with low limit of radius (Fig. 1). This implies that the transition to continual approach is impossible along SWNT perimeter. On the figure the Z axis is directed along nanotube axis and I axis – along SWNT perimeter. We study so-called “zig-zag” or (n, 0) SWNT, where n – a number of hexagons on the tube perimeter. In order to apply Fourier analysis it is assumed the (n, 0) tube is infinite in Z axis direction.

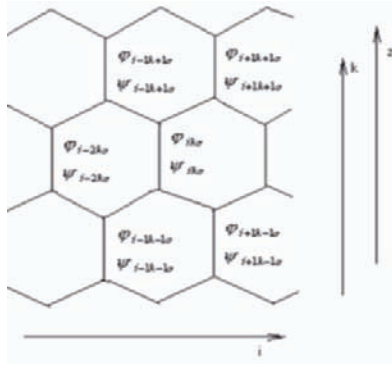


Figure 1. Geometry of the system. Z axis is directed along nanotube axis.

To describe the electronic structure of carbon nanotubes the Hubbard model has been chosen as it can describe the electrical and magnetic properties and high temperature superconductivity effects also [11]. The model includes the terms of the electron jump energy in vicinity approach and the energy of Coulomb’s repulsion of two electrons localized on the same point of unit cell. Hubbard Hamiltonian for the described system is following [11]:

$$H = - \sum_{j\Delta\sigma} t_{\Delta} (a_{j+\Delta\sigma}^+ a_{j\sigma} + a_{j\sigma}^+ a_{j+\Delta\sigma}) + \mu \sum_{j\Delta} a_{j\sigma}^+ a_{j\sigma} + U \sum_j a_{j\sigma}^+ a_{j\sigma} a_{j+\sigma}^+ a_{j-\sigma}, \quad (1)$$

where $a_{j\sigma}^+, a_{j\sigma}$ - the creation and annihilation Fermi operators for an electron on $j=\{i, k\}$ -point (Fig. 1) with spin σ , t_{Δ} – the jump integral, U – the Coulomb repulsion energy of electrons, μ – the chemical potential. The Heisenberg motion equation for Fermi operator of the system with the Hamiltonian (1) is well-known:

$$i\dot{a}_{j\sigma} = [a_{j\sigma}, H] \quad (2)$$

According to Davydov’s method [12, 13] choose the kind of wave function as follow:

$$\begin{aligned} |\Psi(t)\rangle &= V(\tau) |\Psi(0)\rangle = N^{-\frac{1}{2}} \sum_n \alpha_n(\tau) a_n^+ |0\rangle = \sum_n \varphi_n(\tau) a_n^+ |0\rangle \\ |\Psi(0)\rangle &= N^{-\frac{1}{2}} \sum_n a_n^+ |0\rangle \end{aligned} \quad (3)$$

where $V(\tau)$ – the evolution operator, $\psi(0)$ – the ground state wave function of electrons in carbon nanotube, $|0\rangle$ – the vacuum wave function, N – the number of carbon atoms. Then the average of the equations (2) as follow:

$$i \frac{\partial}{\partial t} \langle 0 | a_f(\tau) | \psi(0) \rangle = \langle 0 | [a_f, H] | \psi(0) \rangle,$$

and the follow splitting of operator average values have been used:

$$\begin{aligned} \langle 0 | a_k^+ a_k a_f | \psi(0) \rangle &= \langle 0 | a_f | \psi(0) \rangle - \langle 0 | a_k a_k^+ a_f | \psi(0) \rangle \longrightarrow \\ &\longrightarrow \langle 0 | a_f | \psi(0) \rangle - \langle 0 | a_k | \psi(0) \rangle \langle \psi(0) | a_k^+ | 0 \rangle \langle 0 | a_f | \psi(0) \rangle \end{aligned} \quad (4)$$

$$\text{Further the next notifications } \langle 0 | a_f | \psi(0) \rangle = \varphi_f, \quad \langle \psi(0) | a_f^+ | 0 \rangle = \varphi_f^*,$$

representing non-normal wave functions, are used below. Also, according to [2 - 4], the lattice of SWNT has been separated by two sublattices, so as electrons make jumps between the sublattices. The values corresponding to the different sublattices have been notified by φ and ψ correspondently with the according indexes. Such dissection makes Lorenz invariance of the equations, where the product $t \cdot a$ plays a light velocity role (a – a lattice constant). At the same time the special feature of our method is that we assume the character scales along the axis of the nanotube, for which values $\varphi_{j\sigma}$ and $\psi_{j\sigma}$ change very much, is much larger than the distance between carbon atoms and, consequently, it may be used a continual approach as follows:

$$\varphi_{ik \pm 1\sigma} = \varphi_{ik\sigma} \pm a \frac{\partial \varphi_{ik\sigma}}{\partial z} + \dots, \quad \psi_{ik \pm 1\sigma} = \psi_{ik\sigma} \pm a \frac{\partial \psi_{ik\sigma}}{\partial z} + \dots \quad (5)$$

After applying the continual approximation and restricting only two terms in above expansions the motion equations became following:

$$\begin{aligned} i\dot{\varphi}_{j\sigma} &= -t_0(\psi_{j\sigma} + \psi_{j-1\sigma} + \psi_{j+1\sigma} + a \frac{\partial}{\partial z} \psi_{j-1\sigma} + a \frac{\partial}{\partial z} \psi_{j+1\sigma}) + \mu \varphi_{j\sigma} + U \varphi_{j\sigma} |\varphi_{j-\sigma}|^2, \\ i\dot{\psi}_{j\sigma} &= -t_0(\varphi_{j\sigma} + \varphi_{j-1\sigma} + \varphi_{j+1\sigma} - a \frac{\partial}{\partial z} \varphi_{j-1\sigma} - a \frac{\partial}{\partial z} \varphi_{j+1\sigma}) + \mu \psi_{j\sigma} + U \psi_{j\sigma} |\psi_{j-\sigma}|^2 \end{aligned} \quad (6)$$

To analyze the equations (6) we'll remove the terms containing μ by the following replacement:

$$\psi_{j\pm\sigma} \longrightarrow \psi_{j\pm\sigma} \exp(-i\mu t)$$

and apply Fourier transformation of the equation (6) using periodical boundary conditions along the nanotube perimeter:

$$\begin{aligned} \varphi_{j\sigma} &= N^{-\frac{1}{2}} \sum_k \varphi_{k\sigma} \exp\left(\frac{ikj2\pi}{N}\right), \quad \psi_{j\sigma} = N^{-\frac{1}{2}} \sum_k \psi_{k\sigma} \exp\left(\frac{ikj2\pi}{N}\right) \\ \varphi_{k\sigma} &= N^{\frac{1}{2}} \sum_j \varphi_{j\sigma} \exp\left(-\frac{ikj2\pi}{N}\right), \quad \psi_{k\sigma} = N^{\frac{1}{2}} \sum_j \psi_{j\sigma} \exp\left(-\frac{ikj2\pi}{N}\right) \end{aligned} \quad (7)$$

where N – the number of atoms along the SWNT perimeter, $k \in [0, N-1]$.

Finally the following equations have been obtained:

$$\begin{aligned}
i\dot{\varphi}_{k\sigma} &= -t_0(1 + 2\cos\frac{2\pi k}{N})\psi_{k\sigma} - 2t_0a\cos\frac{2\pi k}{N}(\psi_{k\sigma})_z + \frac{U}{N}\sum_{k_1k_2}\varphi_{k_1\sigma}\varphi_{k_2-\sigma}\varphi_{k_1+k_2-k-\sigma}^* , \\
i\dot{\psi}_{k\sigma} &= -t_0(1 + 2\cos\frac{2\pi k}{N})\varphi_{k\sigma} - 2t_0a\cos\frac{2\pi k}{N}(\varphi_{k\sigma})_z + \frac{U}{N}\sum_{k_1k_2}\psi_{k_1\sigma}\psi_{k_2-\sigma}\psi_{k_1+k_2-k-\sigma}^*
\end{aligned}
\tag{8}$$

These are non-linear equation for the Fourier images of functions φ and ψ which like non-linear Schroedinger equation and require a special solution.

3. Results and Discussion

However the obtained system of the equations remains still too difficult for analyzing. For definiteness the (6,0) SWNT has been studied ($N=6$). To facilitate the solution of the equation system (8) we shall research first of all the case when only one oscillation mode ($k=0$) is induced. Obviously, the case corresponds to the oscillations, which are homogeneous along SWNT perimeter. For further simplification of the equation system we shall suppose that $\varphi_\sigma = \varphi_{-\sigma}, \psi_\sigma = \psi_{-\sigma}$. Using Lorenz's invariance property for running perturbations (its amplitude depends on only $z-vt$ variable), the problem is reduced to the analyze of two ordinary differential equation system. The differential equation system has been solved numerically by the eighth order Runge-Kutt method. So, the typical dependencies of absolute values of $\varphi(z-vt), \psi(z-vt)$ (one-electron wave functions) on $z-vt$ variable are shown in Fig. 2a and its phase portrait is shown in Fig. 2b. The solution of the non-linear equation system looks like the typical regular solution representing the soliton lattice. Notice that the corresponding phase portrait is like the cycle.

The dependencies of the values $\varphi_\sigma(z-vt), \psi_\sigma(z-vt) (\sigma = \pm)$ corresponding to homogeneous oscillations along the nanotube perimeter on variable $z-vt$ are shown in Fig. 3a and corresponding phase portraits are shown in Fig. 3b. Note that the character of the soliton lattices remains constant and phase portraits are also like cycles.

The system (8) becomes closed if we assume that only $k=0, k=3$ or $k=0, k=2, k=4$ modes are induced. In other words the equation system becomes closed for modes in the center and in the middle of the first Brillouin zone and also for modes in the center and in the distance of $1/3$ from the first Brillouin zone. In general, such reduction of the system is caused by the existence of Abelian subgroups in the translation group along the corresponding direction and, perhaps, by bush-modes describing in [14, 15]. So, in the case of $N=6, k=0, k=3$ the reduced system of equations is the following:

$$\begin{aligned}
 i\dot{\phi}_{0\sigma} &= -3t_0\psi_{0\sigma} - 2t_0a(\psi_{0\sigma})_z + \frac{U}{6}\left[\phi_{0\sigma}\left(|\phi_{0-\sigma}|^2 + |\phi_{3-\sigma}|^2\right) + \phi_{3\sigma}(\phi_{0-\sigma}\phi_{3-\sigma}^* + \phi_{3-\sigma}\phi_{0-\sigma}^*)\right] \\
 i\dot{\psi}_{0\sigma} &= -3t_0\phi_{0\sigma} + 2t_0a(\phi_{0\sigma})_z + \frac{U}{6}\left[\psi_{0\sigma}\left(|\psi_{0-\sigma}|^2 + |\psi_{3-\sigma}|^2\right) + \psi_{3\sigma}(\psi_{0-\sigma}\psi_{3-\sigma}^* + \psi_{3-\sigma}\psi_{0-\sigma}^*)\right] \\
 i\dot{\phi}_{3\sigma} &= 2t_0a(\psi_{3\sigma})_z + \frac{U}{6}\left[\phi_{3\sigma}\left(|\phi_{0-\sigma}|^2 + |\phi_{3-\sigma}|^2\right) + \phi_{0\sigma}(\phi_{0-\sigma}\phi_{3-\sigma}^* + \phi_{3-\sigma}\phi_{0-\sigma}^*)\right] + t_0\psi_{3\sigma} \\
 i\dot{\psi}_{3\sigma} &= -2t_0a(\phi_{3\sigma})_z + \frac{U}{6}\left[\psi_{3\sigma}\left(|\psi_{0-\sigma}|^2 + |\psi_{3-\sigma}|^2\right) + \psi_{0\sigma}(\psi_{0-\sigma}\psi_{3-\sigma}^* + \psi_{3-\sigma}\psi_{0-\sigma}^*)\right] + t_0\phi_{3\sigma}
 \end{aligned}
 \tag{9}$$

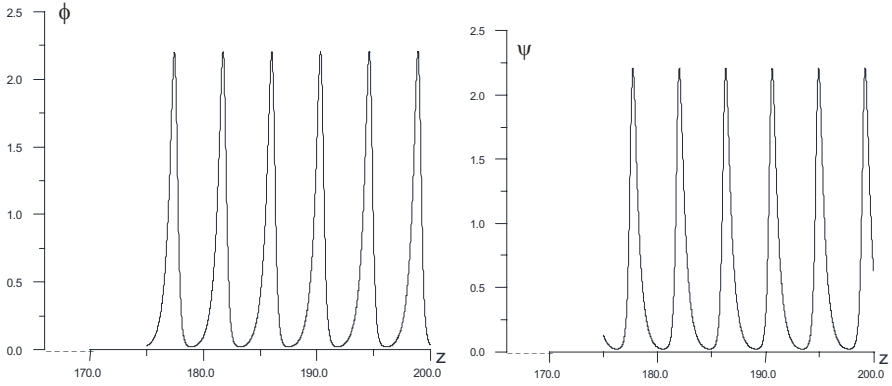


Figure 2a. The dependences of $\phi(z - vt)$, $\psi(z - vt)$ function modules on the argument.

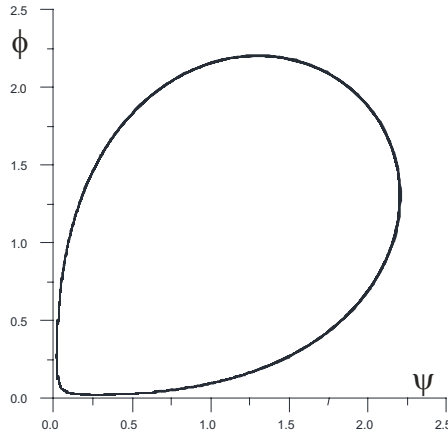


Figure 2b. The phase portrait of $\phi(z - vt)$, $\psi(z - vt)$ modules.

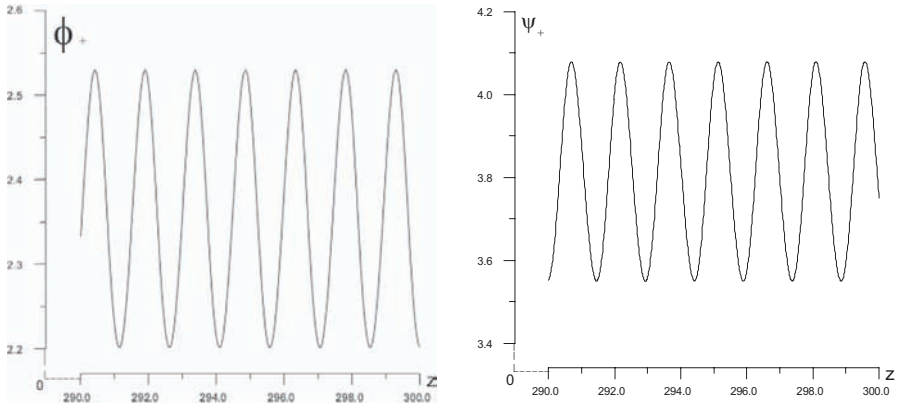


Figure 3a. The dependences of $\varphi_+(z-vt)$, $\psi_+(z-vt)$ function modules on the argument.

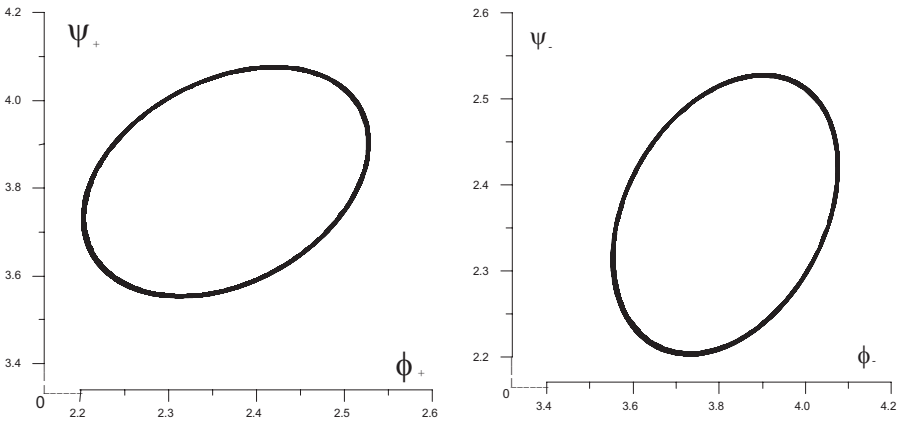


Figure 3b. The phase portraits of $\varphi_{\pm}(z-vt)$, $\psi_{\pm}(z-vt)$ modules.

The case of $k=0$, $k=2$, $k=4$ is not described in this paper because of its complication. The equation numerical solutions for absolute values of $\varphi_{0+}(z-vt)$, $\psi_{0+}(z-vt)$ are shown in Fig. 4a and the corresponding phase portrait is shown in Fig. 4b. Absolute values of $\varphi_{3-}(z-vt)$, $\psi_{3+}(z-vt)$ are shown in Fig. 5a and the phase portrait in the coordinates of absolute values of $\varphi_{3+}(z-vt)$, $\psi_{3+}(z-vt)$ is shown in Fig. 5b. Note in this case the soliton lattices are of more complicated structure appearing in modulation of its amplitude. This fact may be explained by the constant “transfer” of energy from the homogeneous mode to the mode corresponding to Brillouin zone center and back. We’d like to attract your attention to the complicated character of the structure of soliton grids in

Fig. 5a. Such behavior is typical for soliton solutions of non-linear Schroedinger equation, which is closely connected to the model of Hubbard [16]. Also note the cycle in Fig. 4b, such portrait may further be the typical feature of soliton lattice appearance.

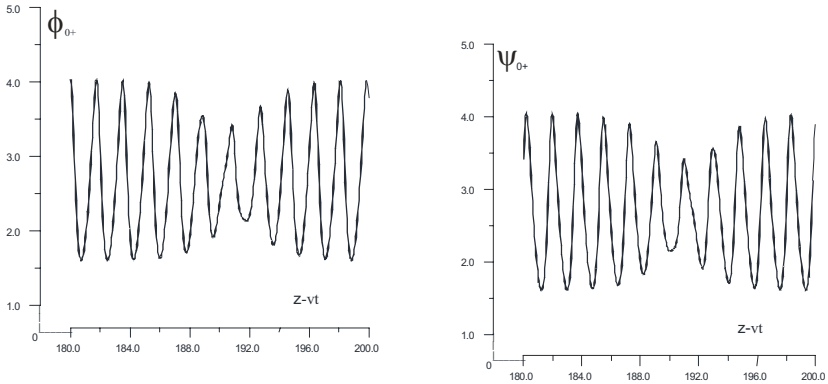


Figure 4a. The dependences of $\phi_{0+}(z-vt)$, $\psi_{0+}(z-vt)$ function modules on the argument.

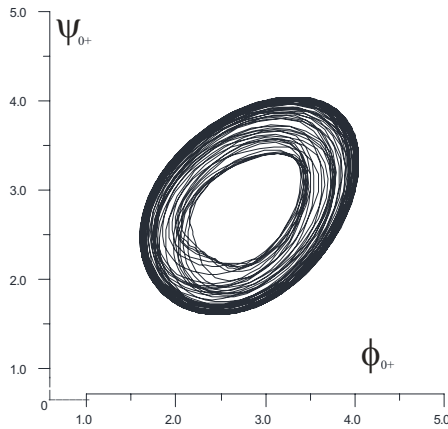


Figure 4b. The phase portrait of $\phi_{0+}(z-vt)$, $\psi_{0+}(z-vt)$ modules.

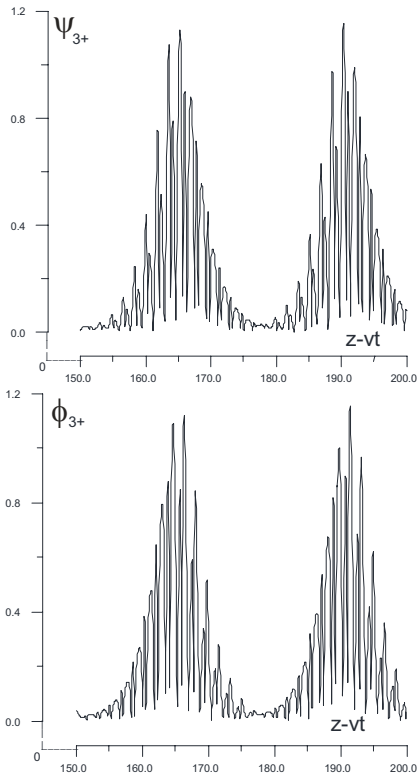


Figure 5a. The dependences of $\phi_{3+}(z - vt)$, $\psi_{3+}(z - vt)$ function modules on the argument.

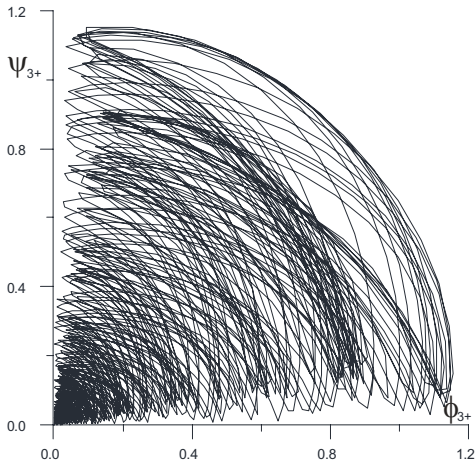


Figure 5b. The phase portrait of $\phi_{3+}(z - vt)$, $\psi_{3+}(z - vt)$ modules.

It is well-known [12, 13] that the balance of dispersion process and nonlinear growth (attenuation) amplitude is necessary for existence of the stable decision of the nonlinear equation. In our case the amplitude increase caused by nonlinear

growth results in change of fluctuation frequency, i.e. results in the frequency dynamic shift being common for all nonlinear systems. In turn the frequency change entails the dispersion change that in general case of balance absence results in the change of the lattice form. One should note that the dynamics of soliton lattice is considered on times being smaller than the characteristic time of attenuation of processes in the system (i.e. the attenuation contribution to the balance of dispersion processes and nonlinear change of the amplitude are possible to be neglected). Besides that in real carbon nanotubes together with non-linearity caused by Coulomb interaction of electrons there is also acoustic elastic non-linearity. The separation of non-linearity's contributions above mentioned in the process of soliton lattice formations represents a difficult task and the contribution of non-linearity from Hubbard Hamiltonian is considered only in the paper. This non-linearity is greatest under the order of size in our model (interaction constant is of 10.0 eV). Qualitatively the correction of acoustic non-linearity can be reduced to the renormalization of Coulomb integral U .

The Figures show that the ϕ , ψ values can be changed rather quickly, that begins to contradict with the assumption that in decomposition (5) it is possible to be limited to first derivative on z . With the aim of the specification of the circumstance the calculations, in which high derivatives on z were also taken into account, have been also carried out. Essential change of values ϕ , ψ has been not revealed.

4. Conclusions

In conclusion we would like to resume the main results.

First, due to some approaching we have obtained non-linear periodical wave functions of electron ion carbon nanotubes, which are presented soliton lattices. We consider soliton lattices of obtained type can be revealed by using the diffraction methods. The research based on these methods will make it possible to determine the parameters of the grids and connect them to the corresponding values in microscopic Hamiltonian. Besides these lattices can modulate sound fluctuations, that it is also necessary to take into account at the study of nanotubes by acoustic methods.

Second, these grids make the regular structure like domain in fact. Here domains are the regions with different electron density. The existence of domain electron structure will contribute to the receptivity of the nanotubes and due to domain structure one may hope to find out the effects of a memory in the electron subsystem of nanotubes. One should to note that the similar domains can play the determining role (due to Coulomb interaction of electrons) in physical properties of as nanotube ropes and multi wall carbon nanotubes.

Third, the existence of regular periodic structure leads, when an additional electron moves along such structure, to quantization of it energy (due to Flocke theorem). The quantization leads to additional energetic levels in carbon nanotube spectrums and may also lead to suppression of electron-phonon interaction (if energy levels enough separate from phonon spectrum) and to increasing of carbon nanotubes conductivity. Especially appreciably it can be shown in case of low temperatures at sufficient electron concentration.

Acknowledgments

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INVESTIGATION OF LOW-TEMPERATURE RADIATION LIVING RADICAL POLYMERIZATION OF VINYL MONOMERS WITH FULLERENE C₆₀ BY OPTICAL SPECTROSCOPY

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Abstract. Water-soluble polymers of acrylamide and acrylic acid with high extent (~90%) of C₆₀ consumption are obtained by technique of low-temperature radiation living radical polymerization. In absorption spectra of these copolymers one can see gradually descended unstructured absorption in the range 240-700 nm, characteristic for fullerene covalent-bound or its clusters. The way of radiation initiation is used to obtain the products of high purity, because it is not necessary to embed into the system any initiators or catalyst. Latter is very important in the case of synthesis of polymers for medical purposes. Also at radiation initiation a rate of initiation reaction does not depend on the temperature and the sterilization of products takes place simultaneously.

Keywords: water soluble polymers, fullerene, low-temperature, γ -radiation, free radicals.

1. Introduction

Fullerenes and their water soluble derivatives are of great deal interest for scientific research due to their biological activity [1]. Therefore, the problems of modification and functionalization of nanomaterials to obtain their water soluble derivatives are very challenging task. In present work we have investigated low-temperature γ - induced copolymerization of vinyl monomers such as acrylamide and acrylic acid with fullerene C₆₀ to obtain their water soluble polymers containing fullerene.

2. Experimental

Polymerization took place during heating of γ -irradiated at 77K by the dose 4 Mrad mixtures of 15% solution of acrylamide (AA) or acrylic acid (Aacid) in ethyl alcohol with solution of fullerene in toluene. So, polymerization has performed in glassy matrix at temperatures a little higher than the temperature of vitrification of alcohol in the regime of overcooled high-viscous liquid ($T_g = 110$ K). In these conditions the mobility of monomer molecules is rather high in order to reach the active center and at the same time the mobility of propagating macroradicals is not enough for recombination [2]. All above said leads to high efficient polymerization. Actually the polymerization yield for pure polyacrylamide (PAA) is around of 98% while for the polymerization of the mixture of acrylamide in alcohol with fullerene in toluene is around of 70%. A yield of pure PAAcid appeared to be 57%, the yield of FPAAcid is 21%. The portion of free fullerene molecules did not participate in polymerization was eliminated by its double extraction by toluene from water solution of polymers obtained.

The fullerenecontaining polymers of acrylamide (FPAA) or acrylic acid (FPAAcid) turned out to be soluble in water and in their optical absorption spectra demonstrate an absorption in region from 240 nm up to 700 nm whereas in

absorption spectra of these pure polymers (PAA) or (PAAcid) there is not any absorption in this range (Figs. 1, 2).

Fullerene containing polymers after elimination of water are represents the yellow colored films. Under hundred-fold enlargement it can be seen that fullerene

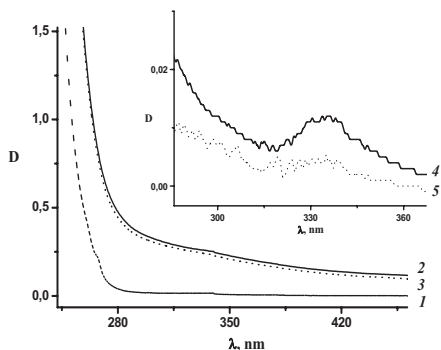


Figure 1. Optical absorption spectra of water solutions of: 1 – PAA (30 mg/ml); 2– FPAA (30 mg/ml) before extraction of free C_{60} or its complexes by toluene; 3 – FPAA after double extraction of free C_{60} or its complexes by toluene; 4 – optical absorption spectrum of first extract by toluene; 5 – optical absorption spectrum of second extract by toluene.

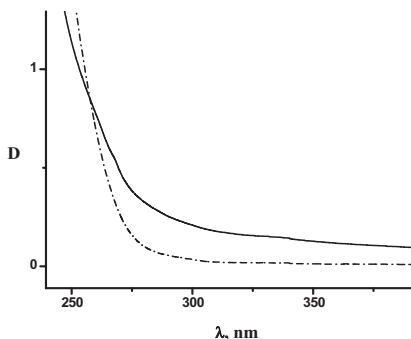


Figure 2. Optical absorption spectra of water solutions of: 1- FPAAcid; 2 – PAAcid.

containing polymers are aggregated into both globes of diameter around 30 micron and into graft dendritic shapes (10×30 micron). The films are easy dissolved in water again. By so doing they remain all features of optical absorption spectra, that is unstructured gradually descending absorption from 240 nm to 700nm characteristic for covalent bound fullerene [3] or its klusters [4]. The copolymer kinetic chain lengths of PFAA and PFAAcid evaluated as a ratio of copolymer yields to yields of radical appeared to be 1.7×10^3 for FPAA and 0.5×10^3 for FPAAcid. That means 1-2 molecules of fullerene are embedded into polymer chain. Actually the number of C_{60} molecules may be more in copolymer molecule due to chain transfer effect observed in [5] for polymerization of PAA in the same conditions.

3. Conclusions

Thus, water - soluble polymers of acrylamide and acrylic acid containing covalent bound fullerene are obtained. These products demonstrate in the optical absorption spectra the unstructured gradually descending absorption in the region from 240 nm to 700 nm characteristic for covalent bound fullerene or its aggregations.

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INFLUENCE OF HYDROGEN ON MAGNETOCRYSTALLINE ANISOTROPY OF TbFe₆Co₅Ti SINGLE CRYSTAL

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Abstract. Single crystals of TbFe_{11-x}Co_xTiH_y ($x = 5$; $y = 0, 1$) with the tetragonal ThMn₁₂-type structure were obtained. Magnetisation measurements along main crystallographic directions of TbFe₆Co₅TiH_y ($y = 0, 1$) single crystals have been performed in the temperature range 5–340 K. It was established that TbFe₆Co₅Ti compounds show "easy axis" anisotropy in whole temperature range below Curie temperature (T_C). It was concluded that hydrogenation leads to an increase of magnetic anisotropy, and TbFe₆Co₅TiH hydride demonstrates "easy plane" anisotropy with the easy axis oriented along the [100] crystallographic direction. It was found that the replacement of the Fe by Co and hydrogen insertion into the crystal lattice of Tb(Fe,Co)₁₁Ti compounds have an opposite influence on the magnetocrystalline anisotropy.

Keywords: rare-earth compounds, hydride, magnetocrystalline anisotropy

1. Introduction

Among the series of rare-earth-transition-metal compounds, the pseudobinary RFe_{12-x}M_x compounds are attractive for technological magnetic applications because they contain a large amount of iron, crystallize with a uniaxial structure and, thus, show uniaxial magnetic anisotropy. This series of alloys adopts the tetragonal ThMn₁₂-type crystal structure (space group I4/mmm). The unit cell contains 26 atoms (two formula units per unit cell). Since the rare-earth ions occupy just one crystallographic site with the tetragonal symmetry (2a), these compounds are particularly suitable to study effects brought about by the presence of incompletely filled 4f shell of the rare-earth ions. For selected R or M, potentially hard magnetic materials are obtained for SmFe₁₁Ti [1–3] and SmFe₁₁TiH [4] where insertion of hydrogen induces an enhancement of the magnetic features. The RFe₁₁Ti compounds have rather high Curie temperatures (T_C) around 600 K. A replace of Fe by Co leads to increase the Curie temperature and a change of magnetocrystalline anisotropy (MCA) of the 3d-sublattice [5–6]. It was established [7], that the rare-earth contribution to the magnetic anisotropy

energy has opposite signs in $\text{RFe}_{12-x}\text{M}_x$ and respective $\text{RCo}_{12-x}\text{M}_x$ as compared with Co contribution. Absorption of hydrogen gas leads to marked changes in the main magnetic properties of these compounds [8].

The magnetic properties of $\text{TbFe}_{11}\text{Ti}$ have been studied on single crystals [5,9]. Competition of magnetic anisotropy of the Tb and Fe sublattices leads to spin-reorientation transition (SRT) at 325 K, where the easy magnetization direction changes from the [100] (at low temperature) to the [001] crystallographic direction [9]. The introduction of hydrogen into the crystalline lattice of $\text{TbFe}_{11}\text{Ti}$ induces easy plane states in whole temperature range below T_C [10]. At Fe replacement by Co the SRT temperature decreases [6]. In the present papers we present the data for $\text{TbFe}_6\text{Co}_5\text{Ti}$ and its hydride in a continuous of our previous work on $\text{Er}(\text{Fe},\text{Co})_{11}\text{TiH}$ hydrides [11].

2. Experimental details

The $\text{TbFe}_6\text{Co}_5\text{Ti}$ alloy was prepared by melting the elements with purity higher than 99.95 % in an induction furnace. Details of the single crystal preparation have been described previously [6]. The metal hydride syntheses were carried out in a high-pressure reactor chamber of a conventional Sieverts-type volumetric system. The samples were activated for 4 hours in vacuum ($4 \cdot 10^{-4}$ Pa) at 670 K. At this temperature high purity hydrogen gas obtained from the LaNi_5H_6 hydrogen storage was admitted at a pressure of 1.2 MPa to the sample. To achieve a good homogenisation, the samples were slowly cooled (about 4 K per hour) down to room temperature. The amount of the absorbed hydrogen was determined from the hydrogen pressure change in the reactor chamber. The hydrogen concentration of $\text{TbFe}_6\text{Co}_5\text{TiH}_y$ was equal about to 1 H atom per formula unit (f.u.), with an accuracy of ± 0.02 H atoms/f.u.

X-ray diffraction investigation (Co-K α radiation) was made on the powder samples for the phase identification both the parent compound and its hydride and to determine the unit cell parameters. The magnetisation measurements were carried out with a SQUID (Quantum Design MPMS 5-S) magnetometer from 5 to 340 K in magnetic fields up to 50 kOe.

3. Results and Discussion

X-ray diffraction measurements show that the ThMn_{12} -type crystalline structure of $\text{TbFe}_6\text{Co}_5\text{Ti}$ compound is retained upon hydrogenation. The introduction of hydrogen atoms increases the lattice constants. It leads to an isotropic volume expansion with the c/a ratio being almost unchanged.

Figures 1 and 2 show the isotherms obtained from the magnetization measurements at different temperatures for $\text{TbFe}_6\text{Co}_5\text{Ti}$ and its hydride, respectively. Unlike $\text{TbFe}_{11}\text{Ti}$, the $\text{TbFe}_6\text{Co}_5\text{Ti}$ single crystal exhibits a uniaxial magnetic anisotropy over the entire studied range of temperatures from 4.2 K to T_C . It is shown that Fe replacement by Co suppresses easy plane anisotropy completely at Co concentration $x = 5$.

The magnetization curves for the $\text{TbFe}_6\text{Co}_5\text{Ti}$ single crystal along the [110] and [100] directions in the basal plane (Fig. 1) show a sharp jump of the magnetization in the temperature below 300 K at the specific threshold field H_{cr} , which increases with temperature in the range 4.2–300 K. This transition is due to the first-order magnetization process (FOMP) [12] and associate with the irreversible rotation of the magnetization vector at $H = H_{cr}$.

As can be seen from Fig. 2, hydrogenation induces easy plane anisotropy in TbFe₆Co₅TiH. The [100] direction becomes easy magnetization axis and critical fields are not observed in the field dependences of the magnetization for TbFe₆Co₅TiH.

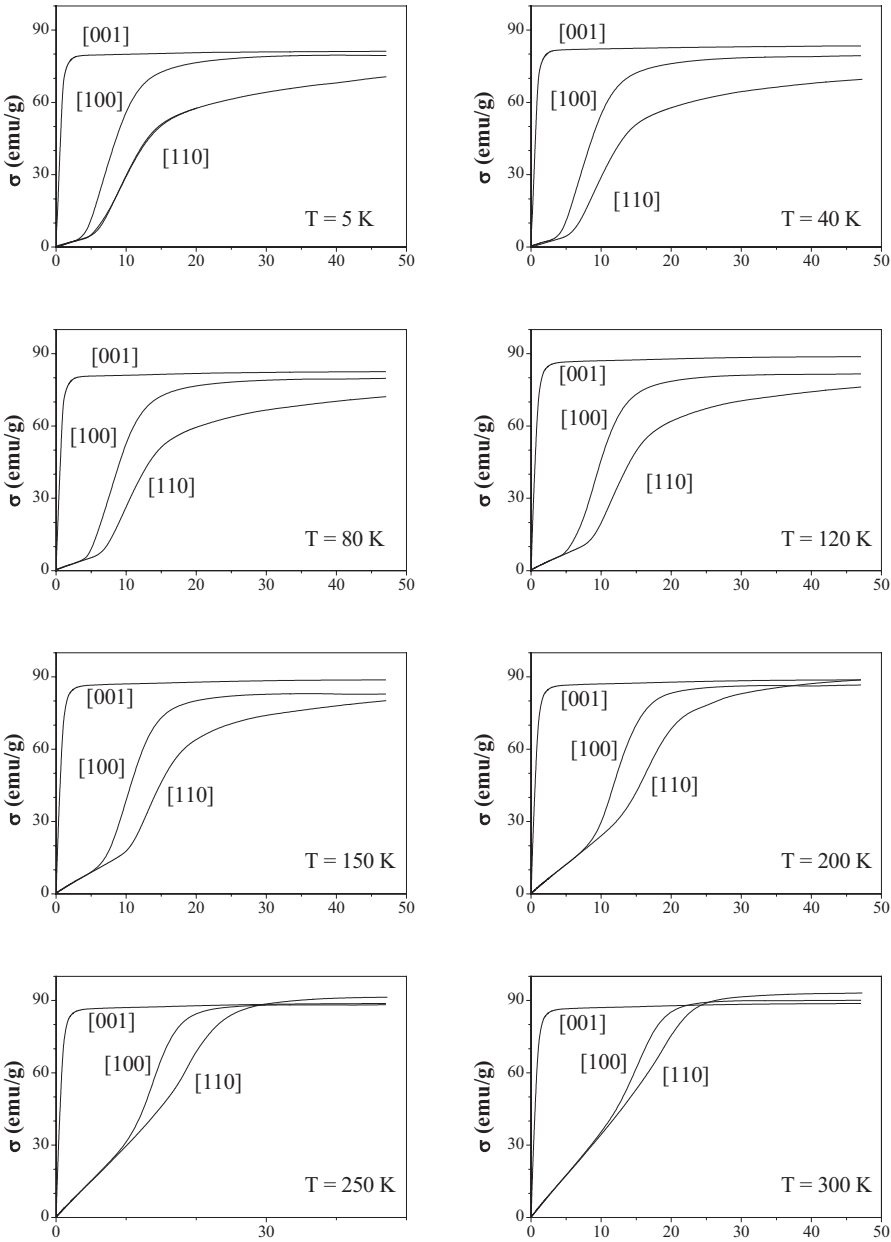


Figure 1. Isothermal magnetization curves of TbFe₆Co₅Ti single crystal for magnetic field along the main symmetry directions at different temperatures.

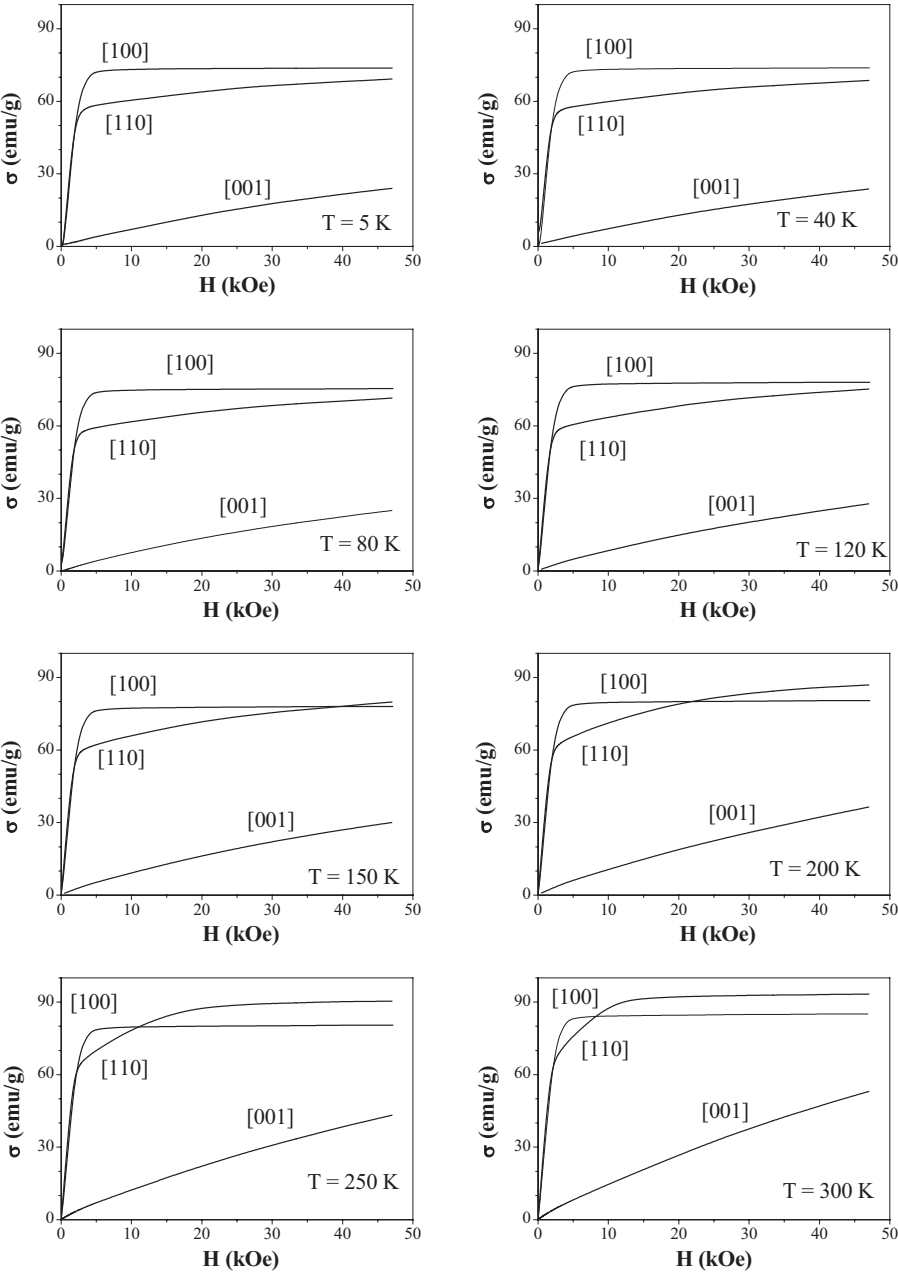


Figure 2. Isothermal magnetization curves of TbFe₆Co₅TiH single crystal hydride for magnetic field along the main symmetry directions at different temperatures.

TABLE 1. Saturation magnetization and anisotropy constants K_1 and K_2 of $\text{TbFe}_6\text{Co}_5\text{Ti}$ and its hydride

Compounds	σ_s (emu/g)		K_1 (10^7 erg/cm 3)		K_2 (10^7 erg/cm 3)	
	5 K	300 K	5 K	300 K	5 K	300 K
$\text{TbFe}_6\text{Co}_5\text{Ti}$	81	88	2.2	0.7	-1.5	-0.1
$\text{TbFe}_6\text{Co}_5\text{TiH}$	74	85	-6.3	-3.4	1.7	0.6

A difference of high field magnetization along various directions can be explained by both high axis MCA and anisotropy of saturation magnetization. At low temperature this effect hides by MCA, but the saturation magnetization anisotropy are observed near 300 K. This behaviour shows that occupation of 3d-band by 3d-collective electrons of Fe-ions differs for various crystallographic directions.

Magnetic anisotropy constants K_1 , K_2 , and K_3 can be found from magnetization curves measured along various crystallographic directions. This method is based on fitting of an experimental magnetization curve $I_{\text{exp}}(H)$ by a calculated dependence $I_{\text{calc}}(H)$, where K_1 , K_2 , K_3 are fit parameters. The values providing the best fit are considered as experimentally obtained constants.

In our work we used Neel phase’s method, which is based on an assumption that a sample can be subdivided into magnetic domains in low magnetic fields. Thus, the total energy E_{total} should also include the energy of the demagnetizing field of a specimen. In this case all the domains contribute to the projection of the magnetization on an external field direction. The advantage of the Neel phase’s method is a more detailed description of magnetization processes [13].

Temperature dependencies of anisotropy constants of $\text{TbFe}_6\text{Co}_5\text{Ti}$ and its hydride are displayed on Figs. 3 and 4, respectively. It can be seen that axial anisotropy constants K_1 and K_2 have a different signs. In both compounds K_1 gives a main contribution to the magnetic anisotropy energy. As can be seen the anisotropy constants (K_1 and K_2) change sign under hydrogenation (see Table 1).

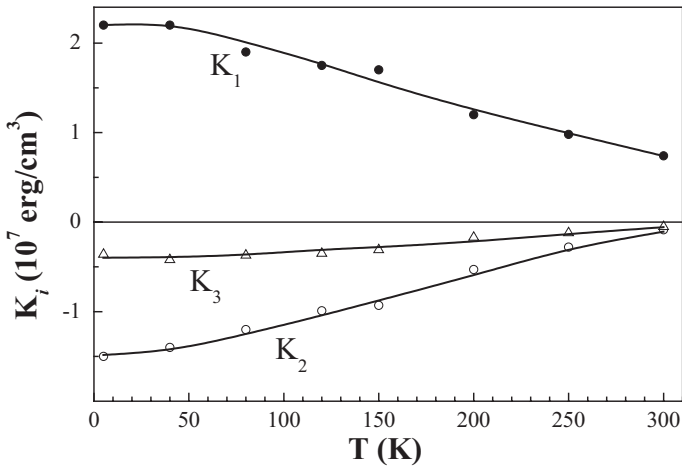


Figure 3. Temperature dependence of anisotropy constants of $\text{TbFe}_6\text{Co}_5\text{Ti}$ compounds.

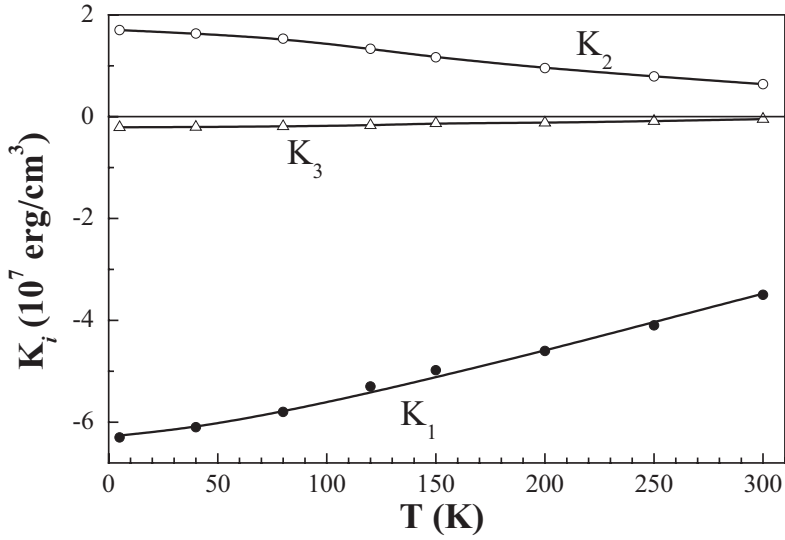


Figure 4. Temperature dependence of anisotropy constants of TbFe₆Co₅TiH hydride.

To understand the magnetic properties of the RFe₁₁Ti compounds, it is important to examine the properties of the 3d sublattice magnetism. To separate magnetic anisotropy of 3d-sublattice, many authors were taken isostructural YFe₁₁Ti compound, where the rare-earth-like Y atom has a closed electron shell and therefore makes no contribution to the anisotropy [14-15]. With increasing cobalt content, magnetic moment deviates from c-axis. From x-ray diffraction measurements of magnetically oriented powder samples, magnetic phase diagram of YFe_{11-x}Co_xTi was obtained [5]. Non-uniaxial anisotropy is observed at low temperature for Co concentration range from x = 6 to 10, where SRT of type “easy plane”-“easy cone” and “easy cone”-“easy axis” were found. The effect of the substitution of Co for Fe on the magnetic anisotropy in YFe_{11-x}Co_xTi (0 ≤ x ≤ 5) single crystals has been studied before [16]. It was found that magnetic anisotropy constants of 3d-sublattice are positive and decrease with Co concentration. Our experimental results show that TbFe₆Co₅Ti become uniaxial, hence, the insertions of Co atoms into TbFe₁₁Ti alloy induces uniaxial anisotropy.

The hydrogen concentration 1 H atom/f.u. corresponds to full occupancy of the interstitial 2b site according to the neutron diffraction experiment [17]. This interstitial site can be seen as a pseudo-octahedron with two rare-earth ions and four iron atoms 8j at the corners. Interstitial atoms occupy 2b sites adjacent to the rare earth, creating a change of crystal field that reflects the local symmetry and inducing significant changes of the MCA.

Hydrogen atoms inserted in TbFe₆Co₅Ti crystal lattice orient quadrupolar moment of the electronic 4f-subshell in an electric field created by a neighbouring ions and electrons along c-axis, that caused to orient of magnetic moment of Tb ion along basal plane. It is well known [4,10], that for the rare-earth ions with Stevens coefficient a_J > 0 (Sm, Er, Yb) the magnetic moment is parallel, while for

the rare-earth ions with $a_J < 0$ (Nd, Tb, Dy, Ho) it is perpendicular to the large axis of the 4f-electron charge cloud. After hydrogenation TbFe₁₁Ti compound retains easy-plane anisotropy in the entire temperature range from 4.2 K to T_C [10]. Similar behavior we found in TbFe₆Co₅TiH_y under hydrogenation. Because of the exchange interaction magnetic moments of Fe and Co orient antiparallel to Tb magnetic moments in basal plane of tetragonal lattice. It can be concluded that magnetocrystalline anisotropy of Tb(Fe,Co)₁₁TiH_y (y = 0, 1) involves in the single ion anisotropy of Tb, Fe and Co ions and Tb-3d exchange anisotropy:

$$K_1 = K_{\text{Tb}} + K_{3d} + K_{\text{Tb-3d}}.$$

4. Conclusion

As indicated earlier [11], the Fe replacement by Co and insertion of hydrogen in Er(Fe,Co)₁₁Ti have opposite change of MCA constants as compared with Tb(Fe,Co)₁₁Ti compounds. If taken into consideration signs of Stevens coefficients for Tb ions ($a_J < 0$) and Er ions ($a_J < 0$), we can conclude that the change of signs of MCA constants K_1 and K_2 under the hydrogen insertion in R(Fe,Co)₁₁Ti crystal lattice and at the Fe replacement by Co correlate with signs of Stevens factors of R ions, that illustrate very important role of the orientation of the quadrupolar moment of the rare-earth 4f-subshell relative to the crystal field gradient.

Acknowledgments

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STUDY OF ISOTOPIC EFFECT FOR HYDROGEN AND DEUTERIUM ADSORPTION ON NANOPOROUS CARBON (NPC) AT 67-78 K

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Abstract. Adsorption isotherms of pure hydrogen and deuterium on samples of nanoporous carbon (NPC) have been determined at range of temperature 67-78 K. Distinction in sorption abilities of nanosorbent in relation to deuterium and to hydrogen has been fixed. Adsorption capacity of the NPC samples relative to deuterium in range of pressure 0-100 kPa is larger than one to hydrogen, and both values are considerably larger than values of hydrogen isotopes adsorption capacity on common sorbents such as zeolites and active carbons.

Separation factors of hydrogen (H_2), hydride of deuterium (HD) and deuterium (D_2) have been determined for adsorption of hydrogen isotopes mixtures on the samples NPC at temperatures 68 K and 78 K. The values don't extremely large. They are close to ones of active carbons.

Keywords: nanoporous carbon, adsorption, gas storage, separation factor, hydrogen, deuterium

1. Introduction

The significant amount of publications is devoted to study of hydrogen sorption on nanoporous carbon materials. High-temperature sorption, which is routinely activated process and results in a chemisorbed state of the bound hydrogen was studied in [1, 2]. Physical adsorption of hydrogen of natural isotopic composition at room and cryogenic temperatures in single-walled carbon nanotubes and others nanostructure materials have been studying a lot of work groups [3-6].

Also, there are theoretical simulations predicted a high adsorption selectivity (up to 100000 at 20 K) of heavy hydrogen isotopes (tritium, deuterium) from isotopes mixtures in nanotubes at low temperatures [7, 8]. But there is no experimental information about adsorption isotherms (except natural isotopic composition hydrogen) and separation factors of the hydrogen isotopic modifications on nanoporous materials at cryogenic temperatures in the literature, and it obtaining has doubtless interest.

2. Experimental

In the majority of cases nanoporous materials exist in a highly dispersed state (seldom - as films). It limits practical application of these materials and in many cases makes difficult for study of their properties. Samples of the nanoporous carbon (NPC) used in this work are produced as a body of cylinder shape with a sufficient mechanical strength. They synthesized by heat treatment of carbide silicon and carbide titanium in chlorine have been studied in the present work. The samples of materials are characterized by the advanced structure of pores, which contains two types of pores: macropores (with the sizes in a few micron) and nanopores with sizes about 0.8 nm. Surface area and volume of pores NPC with

matrix from SiC are 900 cm³/g and 0.44 m²/g, from TiC are 1200 cm³/g and 0.39 m²/g [7].

Pure natural isotopic composition hydrogen (protium), deuterium (atomic concentration of deuterium 99.9 %) and their mixture (1:1) were used as adsorbate in the experiments.

An analysis of the hydrogen isotopic composition and impurity level was carried out by a method of gas chromatography. Impurity level did not exceed $3 \cdot 10^{-4}$ %. Absolute error of definition of deuterium atomic concentration in gas for the region of high deuterium concentrations (>98%) is 0.05%, for wide region of concentrations - up to 0.5%.

Samples of nanoporous carbon were preliminarily crushed till the sizes of 1-5 mm and placed in an adsorption cell. The adsorbents were previously reactivated for 4 hours at the temperature of 680 K and at the pressure of 1 Pa. Before each cycle of measurements the samples of NPC were made a regeneration within two hours with heating of adsorbent, and vacuum degassing of all volume of installation up to residual pressure ~ 0.1 Pa. Background (residual) pressure in system at cooling adsorbent up to boiling point of liquid nitrogen (without delivering adsorbate) did not exceed $8 \cdot 10^{-3}$ Pa.

The equilibrium adsorption isotherms of protium and deuterium were measured volumetrically at temperatures within 67-78 K in the pressure range from 10 Pa to 0.2 MPa. The adsorption cell was cooled in liquid nitrogen boiling under vacuum. The error of determination of adsorbent capacity is not above ± 2 cm³.

The separation factor of H₂, HD and D₂ molecules on samples of NPC at adsorption of hydrogen isotopes mixture was determined by method of single equilibration gaseous and adsorption phase. The isotope composition of the gaseous phase and the adsorption phase was determined using gas chromatograph. The equilibrium between adsorption and gas phases wasn't broken, and change of gas composition in system didn't take a place at the time of taking of gas phase sample, as volume of gas sample was very small, about 0.1 cm³ (total gas volume in system was about 1000 cm³). The composition of adsorption phase was measured after removing of gas phase and desorption of gas out of NPC. The separation factor between components 1 and 2 was calculated by formula:

$$\alpha_{1-2} = \frac{A_1 G_2}{A_2 G_1} \quad (1)$$

where A_i, G_i are concentrations of i-component in adsorption and gas phase.

Several series of measurements of NPC adsorption capacity were carried out. Their results agree well with themselves.

3. Results

3.1. ADSORPTION ISOTHERMS

It was established that the temperature of regeneration of NPC within the limits of 473-673 K does not influence on adsorption capacity of NPC with respect to protium and deuterium. Hydrogen and deuterium are completely desorbed from the sample of NPC at temperature 470-480 K. Adsorption capacity of NPC samples is 10-15 cm³ hydrogen on 1g adsorbent at room temperature and under atmosphere pressure.

Adsorption isotherms of protium and deuterium on the samples of nanoporous carbon adsorbent at temperature 67-78 K are shown on Figures 1 and 2. The capacity of nanoporous carbon adsorbent on deuterium exceeds capacity on protium in all the investigated pressure range. The difference between adsorption value of deuterium and hydrogen is increased with rising of pressure.

Form of protium and deuterium adsorption isotherms on the sample of nanoporous carbon are similar to ones on activated carbon and zeolites. Their comparison is shown in figure 3. You can see that adsorption capacity of the NPC samples is larger than one on common sorbents such as zeolites [10-11] and it is close to active carbon [12].

Adsorption on microporous solids can be described by Dubinin's equation:

$$a = a_0 \exp \left[-BT^2 \left(\ln \left(\frac{T^2 P_{kr}}{T_{kr}^2 P} \right) \right)^2 \right] \quad (2)$$

where a is the total adsorbed gas, cm^3/g , a_0 is the limiting value of sorption, cm^3/g , T , P —temperature and pressure of adsorption, T_{kr} , P_{kr} —critical parameters of gas, B —structured constant of adsorbent surface, K^{-2} .

We expected that the adsorption isotherms could be described with help of Dubinin's equation, but analysis of adsorption isotherms was shown that ones have a breaking of line in region of low pressure and this single-parameter equation isn't able to describe them exactly.

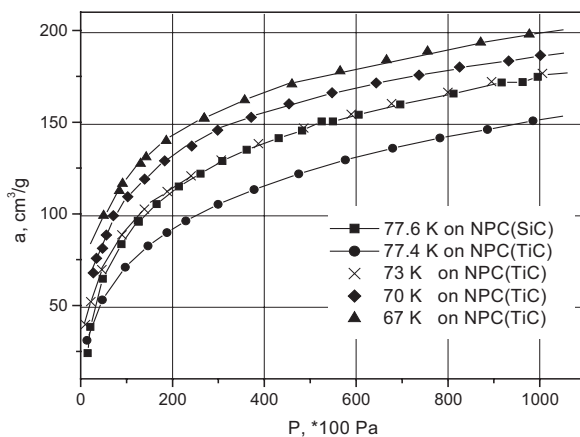


Figure 1. Adsorption isotherms of protium on samples of NPC.

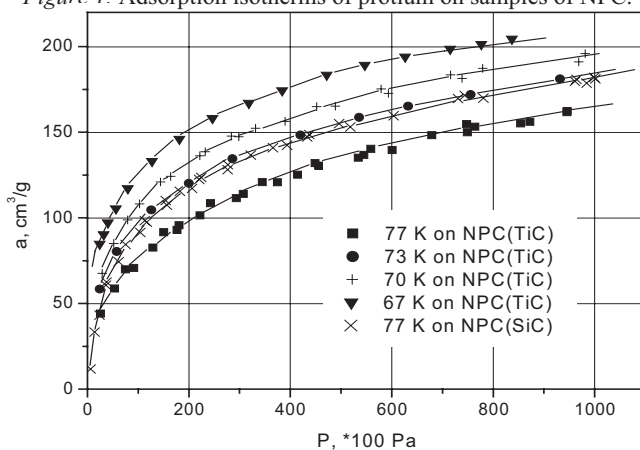


Figure 2. Adsorption isotherms of deuterium on samples of NPCI.

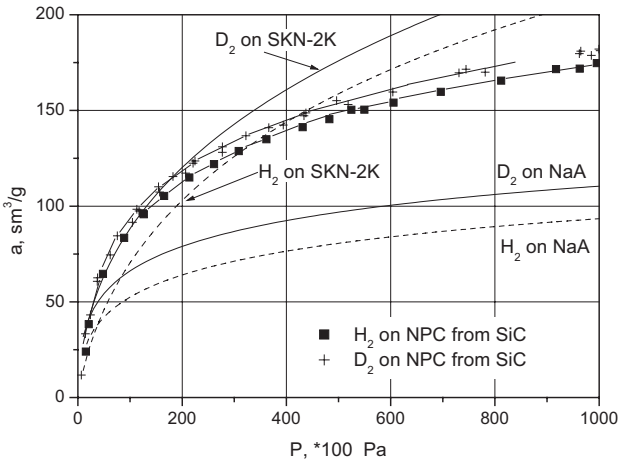


Figure 3. Adsorption isotherms of protium and deuterium on different sorbents at 78 K.

Experimental data for obtained in the present work for adsorption of H₂ and D₂ on NPC have been treated in coordinates of equation (2). For pressure more then 20 kPa parameters of equation (2) are given in Table 1. These values were calculated from experimental data obtained within relatively narrow range of pressure and so they are just synthetic coefficients, not constants.

TABLE 1. Parameters of equation (2) for adsorption H₂ and D₂ on nanoporous carbon for pressure more then 20 kPa

NPS from	T, K	Hydrogen		Deuterium	
		a ₀ , cm ³ /g	B×10 ⁻⁵ , K ⁻²	a ₀ , cm ³ /g	B×10 ⁻⁵ , K ⁻²
TiC	66.7	280.3	0.5005		
	67.0			296.4	0.4872
	69.9	280.2	0.4915	298.1	0.5295
	72.8			287.9	0.4997
	73	270.2	0.4839		
	77.6	252.3	0.4815	282.2	0.5155
SiC	77	290.4	0.4563	300.8	0.4562

3.2. SEPARATION FACTORS OF H₂, HD, D₂ MOLECULES

In this work the separation factors of H₂, HD, D₂ molecules on the samples of NPC were measured at 68 K and 78 K and pressure about 100 kPa for the first time. Average results of several measurement series are presented in Table 2.

The separation factor of hydrogen isotopes on NPC is a bit larger than one is on common activated carbon [12] at the same temperature, but smaller than on zeolites [11].

TABLE 2. Separation factors of hydrogen isotopes on NPC

NPC from	T, K	D ₂ -H ₂	D ₂ -HD	HD-D ₂
SiC	78	1.35±0.25		
TiC	78	1.32±0.03	1.15±0.04	1.14±0.04
	68	1.43±0.02	1.18±0.02	1.21±0.02

Acknowledgements

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MODELING OF DEHYDRATION AND DEHYDROGENATION IN ZIRCONIA WITH ANION IMPURITY

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Abstract. The present work is devoted to research of influence anion impurity (B, C, N, O, F, Ne) on binding energy of hydrogen of hydroxyl group of bridge type on surface zirconia nanocrystal particle and energy of dehydration molecule of water of bridge type with its surface. The analysis of results quantum-mechanical modelling of processes dehydrogenation and dehydration is carried out within the framework of the theory of the SPD-connected systems.

At dehydrogenation hydroxyl group of bridge type an anion impurity boron, carbon and nitrogen increase binding energy of hydrogen with a surface, but impurity of fluorine and a neon reduce energy of connection of hydrogen with a surface zirconia. Impurity boron, carbon and nitrogen reduce an energy barrier of process dehydration from surface zirconia, but impurity fluorine and neon on the contrary increase it.

Keywords: dehydration, dehydrogenation, nanoparticles, zirconia, anion impurity, hydrogen, tight-binding theory, electronic structure.

1. Introduction

New developments in the quantum chemistry methodology, make it possible to obtain new data concerning the electronic structure of surface of zirconia nanoparticle and the dopants in it.

Earlier we had been constructed quantum-mechanical models diamond [1] and oxide [2] nanoparticles with use of the tight-binding theory [3] and influence of hydrogen on electronic structure has been considered. The our work [2] was dedicated to the cell simulation of the electronic structure of 26 impurity d-elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au) of Y-stabilized zirconia nanolayers.

On the basis of these models within the framework of computer modeling of processes in works [4-6] we estimated influence cation S and D impurity elements on energy of connection of hydrogen with zirconia nanoparticles.

The present work is devoted to research of influence anion impurity (B,C,N,O,F, Ne) on binding energy of hydrogen and water with a surface zirconia nanocrystal particle.

These problems are considered within the framework of the cluster model. During simulation the impurity is placed in the substituting anion site.

2. Molecular-orbital treatment

We use the tight-binding theory [7-9]. In the theory of SPD-bonded systems the electronic eigenstates are written in terms of a basis set consisting of a single S state, five D states of each metal atom, three P states on each anion atom of

zirconia and one S state on each hydrogen atom. In the given work, we use parameters containing values for diagonal terms of zirconia covered by hydrogen $\varepsilon_s = -5.68 \text{ eV}$, $\varepsilon_d = -8.46 \text{ eV}$, $\varepsilon_p = -14.13 \text{ eV}$, $\varepsilon_{sH} = -13.55 \text{ eV}$.

On different atoms these orbitals are assumed orthogonal. However atomic orbitals are not eigenfunctions of the considered quantum-mechanical system, as the Hamiltonian matrix elements between orbitals of various atoms are not equal to zero and we use, for account of diagonal elements, the data [7] for energy of s- and d- states of elements.

The matrix elements of sp- and pd-type were considered on the basis of the pseudo-potential theory for transition metals from [7].

To find the eigenfunctions and eigenvalues of the system energy, it is necessary to diagonalize the symmetric matrix $H_{\mu\nu}$.

One of oxygen on a surface of zirconia nanoparticle has the neighbor one atom of hydrogen, forming hydroxyl group OH of bridge type, or two atoms of hydrogen, forming water of bridge type. One-electronic wave functions in a particle without anion impurity were searched as decomposition on nuclear functions which can be submitted as

$$\Phi_\alpha = \sum_j^{NZr} (c_s^j | 5s^j \rangle + \sum_{k=1}^5 c_{p_k}^j | 4d_k^j \rangle) + \sum_j^{NO} \sum_{i=1}^3 c_{p_i}^j | 2p_i^j \rangle + \sum_j^{NH} (c_s^j | 1s^j \rangle$$

where NZr - number of zirconium atoms;

NO - number of oxygen atoms;

NH - number of hydrogen atoms;

i - runs value of three coordinate axes.

$c_{v\alpha}$ - the solutions of the one-electronic equations for a cluster:

$$\sum_v^n (H_{\mu\nu} - \delta_{\mu\nu} E_\alpha) c_{v\alpha} = 0, \quad \alpha = 1, 2, \dots, n$$

where E_α - one-electronic own energy value of cluster; $H_{\mu\nu}$ - matrix elements between atomic orbitales.

Anion impurity atom placed in the next unit anion sublattice considered nanoparticle on a place of one of atoms of oxygen. One-electronic wave functions in a particle with anion an impurity were searched as decomposition on nuclear functions which can be submitted as:

$$\Phi_\alpha = \sum_j^{NZr} (c_s^j | 5s^j \rangle + \sum_{k=1}^5 c_{p_k}^j | 4d_k^j \rangle) + \sum_j^{NO} \sum_{i=1}^3 c_{p_i}^j | 2p_i^j \rangle + \sum_{i=1}^3 c_{p_k}^A | n_A p_i \rangle + \sum_j^{NH} (c_s^j | 1s^j \rangle$$

where $|n_A p_i\rangle$ p- orbital of anion impurity.

3. Dehydrogenation for three-coordinated the oh-groups

We used a cluster of 25 atoms (8 Zr atoms, 1 A atom, 15 O atoms and 1 H atoms): for calculation of energy levels of the zirconia nanoparticle with hydroxyl group of bridge type (Fig. 1). The chemical formula of the cluster can be written down as $Zr_8AO_{14}(OH)$, where (A = B, C, N, O, F, Ne).

The band structure of ZrO_2 has the forbidden gap. Thus electrons from d-levels pass on p- levels of oxygen, providing the ionic character.

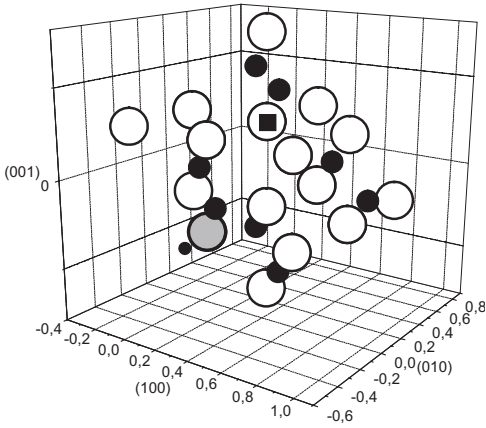
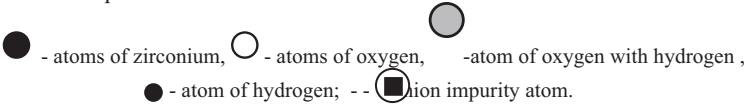


Figure 1. The structure of three-coordinated (bridge type) hydroxyl group on a surface (111) crystal zirconia nanoparticle.



For zirconia without anion impurity, orbital connected with hydrogen is absent in the forbidden gap and appear in the conduction band (Figs. 2-6 on the left side). Thus, hydrogen on surface of zirconia must be shallow donor (i.e. with one donor electron on the each hydrogen).

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution boron was show in Fig. 2 on the right side.

For zirconia with hydroxyl group of bridge type and anion boron, orbital connected with boron appear in the forbidden gap. Thus, zirconia with anion boron and hydrogen on surface can be acceptor or deep donor.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution carbon was show in Fig. 3 on the right side.

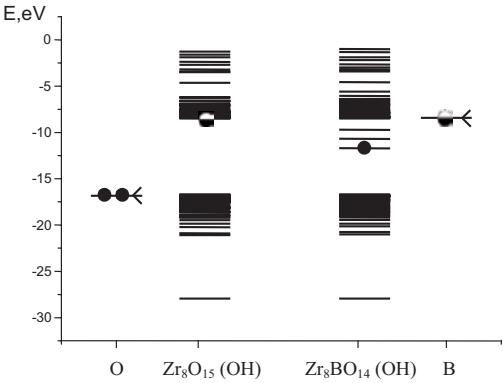


Figure 2. Energies of the one-electron MO's for hydrogen on surface of nanocrystal zirconia particle with boron and without it.

For zirconia with hydroxyl group of bridge type and anion carbon, orbital connected with carbon appear in the forbidden gap. Thus, zirconia with anion carbon and hydrogen on surface can be acceptor or deep donor.

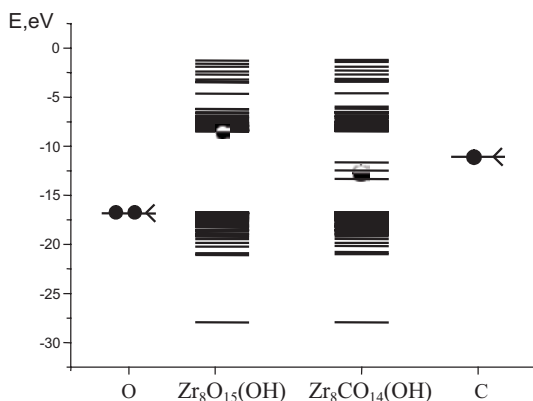


Figure 3. Energies of the one-electron MO's for hydrogen on surface of nanocrystal zirconia particle with carbon and without it.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution nitrogen was show in Fig. 4 on the right side.

For zirconia with hydroxyl group of bridge type and anion carbon, orbital connected with carbon appear in the forbidden gap. Thus, zirconia with anion carbon and hydrogen on surface can be acceptor or deep donor.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution nitrogen was show in Fig. 4 on the right side.

For zirconia with hydroxyl group of bridge type and anion nitrogen, orbital connected with nitrogen appear in the forbidden gap. Thus, zirconia with anion nitrogen and hydrogen on surface must be deep donor.

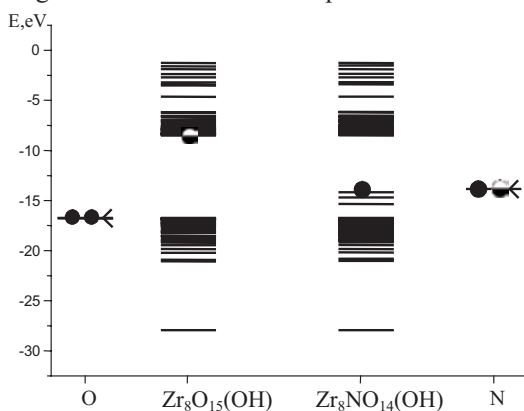


Figure 4. Energies of the one-electron MO's for hydrogen on surface of nanocrystal zirconia particle with nitrogen and without it.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution fluorine was show in Fig. 5 on the right side.

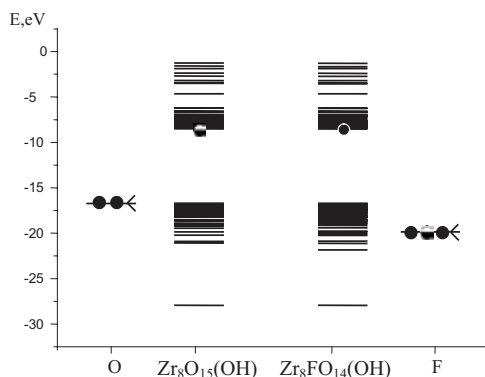


Figure 5. Energies of the one-electron MO's for hydrogen on surface of nanocrystal zirconia particle with fluorine and without it.

For zirconia with hydroxyl group of bridge type and anion fluorine, orbital connected with fluorine is absent in the forbidden gap and electrons appear in the conduction band. Thus, zirconia with anion fluorine and hydrogen on surface must be shallow doubly donor (i.e. with two donor electrons on the each defect).

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution neon was show in Fig. 6 on the right side.

For zirconia with hydroxyl group of bridge type and anion neon, orbital connected with neon is absent in the forbidden gap and electrons appear in the conduction band. Thus, zirconia with anion neon and hydrogen on surface must be shallow threefold donor (i.e. with three donor electrons on the each defect).

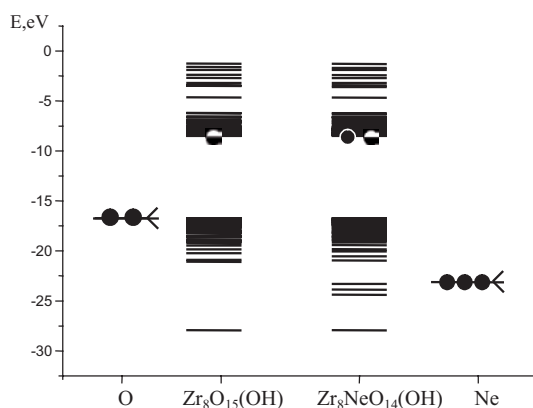


Figure 6. Energies of the one-electron MO's for hydrogen on surface of nanocrystal zirconia particle with neon and without it.

For zirconia with hydroxyl group of bridge type and anion neon, orbital connected with neon is absent in the forbidden gap and electrons appear in the conduction band. Thus, zirconia with anion neon and hydrogen on surface must be shallow threefold donor (i.e. with three donor electrons on the each defect).

A rough estimate of the bonding energy for the hydrogen and zirconia particle can be obtained by monitoring the total energy of the cluster at removing hydrogen. As described in [5] a measure of the total energy of the system is given by the sum of the energies of all the occupied one-electron molecular orbitals. That is,

$$E_{tot} \cong \sum n_i \epsilon_i,$$

where ϵ_i is the energy and n_i is the occupancy number of the i -th orbital.

TABLE 1. Change energy of dehydrogenation at anion doping

Anion impure	B	C	N	F	Ne
Change bonding energy, eV	+0,76133	+0,7617	+0,76179	-0,75793	-0,75455

As calculations show, the activation energy of dehydrogenation from bridge hydroxyl group of nanocrystal zirconia particle change at anion doping.

The results are shown in the Table 1.

4. Dehydration for three-coordinate the water

At research of dehydration it was considered crystal zirconia nanoparticle with a molecule of water also bridge type in place of hydroxyl group. We used a cluster of 26 atoms (8 Zr atoms, 1 A atom, 15 O atoms and 2 H atoms): for calculation of energy levels of the zirconia nanoparticle with hydrogen. The chemical formula such cluster can be written down as $Zr_8AO_{14}(OH_2)$ (Fig. 7).

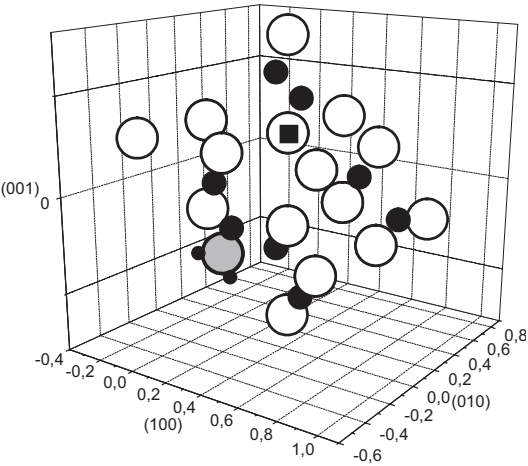
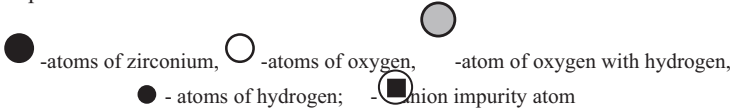


Figure 7. The structure of three-coordinated (bridge type) water on a surface (111) crystal zirconia nanoparticle.



For zirconia with a molecule of water bridge type without anion impurity, orbital connected with water appear in the forbidden gap (Figs. 8-12 on the left side). Thus, water on surface of zirconia must be deep double donor (i.e. with two donor electrons on the each water).

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution boron was show in Fig. 8 on the right side.

For zirconia with water bridge type and anion boron, orbital connected with boron appear in the forbidden gap. Thus, zirconia with anion boron and water on surface can be deep donor.

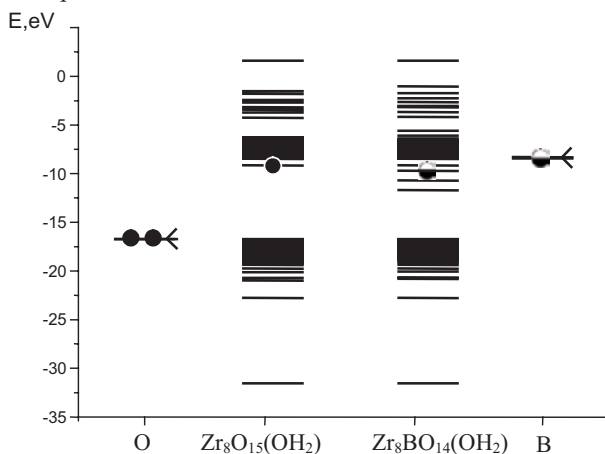


Figure 8. Energies of the one-electron MO's for water on surface of nanocrystal zirconia particle with boron and without it.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution carbon was show in Fig. 9 on the right side.

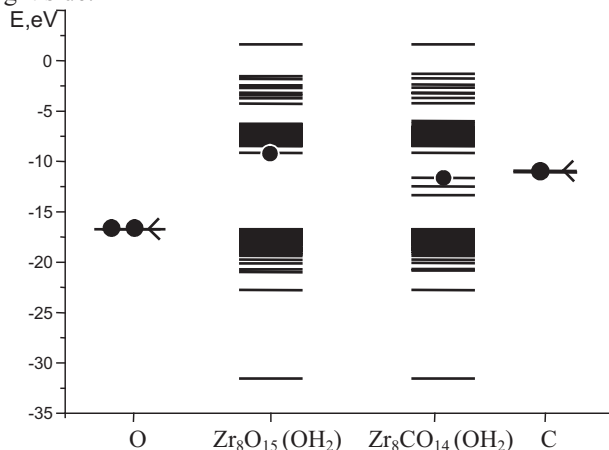


Figure 9. Energies of the one-electron MO's for water on surface of nanocrystal zirconia particle with carbon and without it.

For zirconia with water bridge type and anion carbon, orbital connected with carbon appear in the forbidden gap. Thus, zirconia with anion carbon and water on surface can be acceptor or deep donor.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution nitrogen was show in Fig. 10 on the right side.

For zirconia with water bridge type and anion nitrogen, orbital connected with nitrogen appear in the forbidden gap. Thus, zirconia with anion nitrogen and water on surface must be deep donor. The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution fluorine was show in Fig. 11 on the right side.

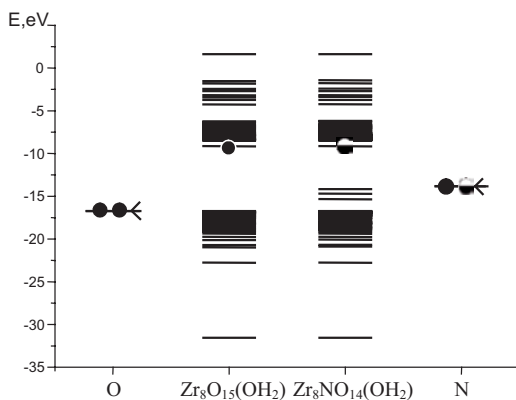


Figure 10. Energies of the one-electron MO's for water on surface of nanocrystal zirconia particle with nitrogen and without it.

For zirconia with water bridge type and anion fluorine, orbital connected with fluorine is absent in the forbidden gap and electrons appear in the conduction band. Thus, zirconia with anion fluorine and water on surface must be shallow donor (i.e. with one donor electron on the each defect).

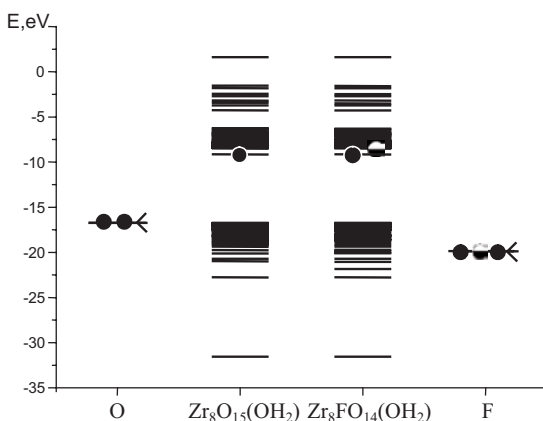


Figure 11. Energies of the one-electron MO's for water on surface of nanocrystal zirconia particle with fluorine and without it.

The one-electron molecular-orbital energies resulted from the calculations when the oxygen atom of the cluster is replaced by substitution neon was show in Fig. 12 on the right side.

For zirconia with water bridge type and anion neon, orbital connected with neon is absent in the forbidden gap and electrons appear in the conduction band. Thus, zirconia with anion neon and water on surface must be shallow double donor (i.e. with two donor electrons on the each defect).

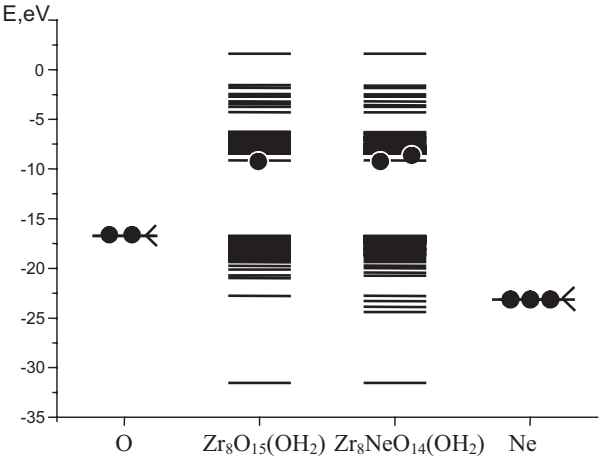


Figure 12. Energies of the one-electron MO's for water on surface of nanocrystal zirconia particle with neon and without it.

As calculations show, the activation energy of bridge dehydration from nanocrystal zirconia particle change at anion doping.

The results are shown in the Table 2.

TABLE 2. Activation energy of dehydration at anion doping

	B	C	N	O	F	Ne
Activation energy, eV	1.20268	1.20282	1.21623	1.23016	1.28883	1.34786

5. Conclusions

1. The analysis of results quantum-mechanical modeling has shown, that at dehydrogenation hydroxyl group of bridge type an anion impurity boron, carbon and nitrogen increase binding energy of hydrogen with a surface, but impurity of fluorine and a neon reduce energy of connection of hydrogen with a surface zirconia.

2. At dehydration molecule of water of bridge type quantum-mechanical modelling has shown qualitatively opposite influence anion impurity. Impurity boron, carbon and nitrogen reduce an energy barrier of process dehydration from surface zirconia, but impurity fluorine and neon on the contrary increase it. However it is necessary to note, that the value of these changes on the order concedes to changes of energy at dehydrogenation.

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STUDY OF Fe-MgO CATALYST STRUCTURAL TRANSFORMATIONS IN THE PROCESS OF PYROLYTIC SYNTHESIS OF CARBON NANOMATERIALS

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Abstract. A chemical composition and structural parameters of specially prepared catalyst for the pyrolytic synthesis of carbon nanomaterials have been studied by X-ray diffraction, Mossbauer spectroscopy and electron microscopy. A plenty of chemical transformations in the catalyst have been monitored. The inert ($\text{Mg}_{1-x}\text{F}_x\text{O}$) and active, very fine particles of the catalyst (MgFe_2O_4) components which are involved in the process of carbon nanofibers were revealed.

Keywords: carbon nanomaterials, Fe-MgO catalyst, Mossbauer spectroscopy, pyrolytic synthesis, X-ray diffraction

1. Introduction

There are a few main methods of carbon nanotube and nanofibre synthesis. The most commonly used amongst them are sublimation of graphite with subsequent desublimation and pyrolysis of hydrocarbons. The pyrolysis does not demand so high temperatures as needed for graphite sublimation, is not connected with high level of energy consumption, and can be realized using cheap raw materials in standard chemical equipment. Relatively low synthesis temperature predetermines moderate level of nontubular forms of carbon admixture concentration: in the course of nanofibre synthesis this level can be lowered to 1 – 3% (during electric arc synthesis it is equal up to 50 – 60%) [1].

In all the cases the carbon nanomaterial is formed in the presence of catalysts – Fe, Co, Ni or alloys of these metals [2].

One of the features of the catalysts for production of carbon nanofibers and especially nanotubes consists in a big role of catalyst particle size besides the catalyst chemical composition. The size can not be assigned in advance, and only the change of synthesis method or synthesis condition allows to produce the most active particles. Chemical composition of the catalyst can be changed during pyrolysis.

The aim of our study is to investigate the chemical composition of the prepared catalyst Fe-MgO and to monitor structural changes of the catalyst during the pyrolysis of methane.

2. Experimental

Pyrolytic synthesis was carried out on gravimetric installation at the temperature 900 °C. The catalytic mixture Fe and Mg with mutual ratio 20:80 was prepared from homogeneous $\text{Fe}(\text{NO}_3) \times 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3) \times 6\text{H}_2\text{O}$ mix with a citric acid and placed on 15 minutes in the furnace heated up to the temperature 600 °C. The rests of the catalyst after pyrolysis were washed in hydrochloric acid. The control of pyrolysis products (nanofibers) morphology was performed by means of electron microscopy (Fig. 1). Structural researches of the catalyst samples before (sample 1) and after the synthesis (sample 2), and also the washed product (sample 3) were carried out by means of X-ray diffraction and Mossbauer spectroscopy. X-ray diffractions patterns have been obtained at Rigaku D/Max diffractometer with Cu K α radiation and graphite monochromator. The estimation of the nanoparticles sizes was performed from line broadening analysis using the Selyakov – Sherrer method.

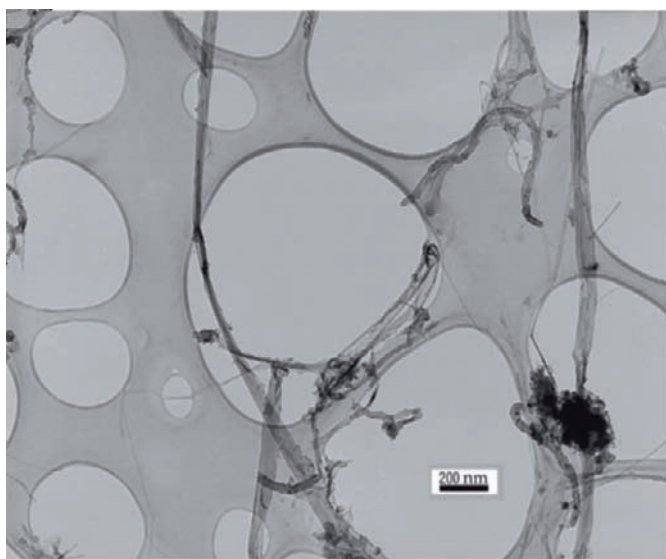


Figure 1. TEM microphoto of pyrolysis synthesis products obtained with Fe-MgO catalyst.

Mossbauer spectra were obtained at 300 K and 80 K using constant acceleration spectrometer with Co 57 (Rh) source and fitted by means of the UnivemMS software.

3. Results and Discussion

X-ray diffraction patterns of three obtained samples are plotted in Fig. 2. Their phase analysis showed follows. The pattern of pure catalyst sample (Fig. 2a) contains the structural peaks of magnesium oxide MgO, and also the weak, strongly widened peaks which correspond to MgFe_2O_4 . Calculated MgO particles

sizes ranges are from 20 to 30 nm. Particles of MgFe_2O_4 have, accordingly, smaller sizes. It is impossible to estimate them precisely because of higher order reflexes weakness. The parameter of MgO lattice has increased on 0,015 Å in comparison with pure Mg oxide. It testifies that some Fe is dissolved in the MgO lattice.

The diffraction pattern of the catalyst sample after synthesis (sample 2) is shown in Fig. 2b. It allows to look after chemical transformations happened in the catalyst during the synthesis. Besides the structural maxima belonging to MgO and MgFe_2O_4 , we can see here the peaks of formed on the catalyst new phases: Fe_3C , γ -Fe and graphite. The calculated lattice parameter of MgO for this sample is slightly larger (0,01 Å) than the same parameter for the sample 1. It corresponds to additional iron penetration in MgO lattice.

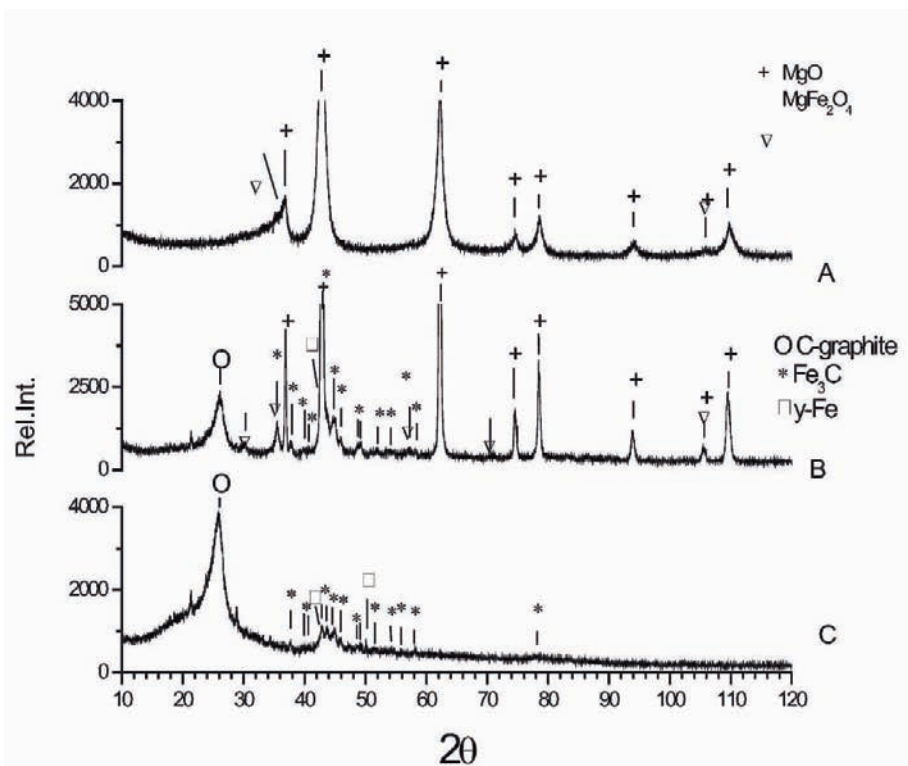


Figure 2. X-ray diffraction patterns of samples: 2a - initial catalyst, 2b - catalyst with formed on it carbon nanostructures, 2c - washed carbon nanostructures.

X-rays diffraction picture of washed sample 3 (Fig. 2c) contains intensive and wide asymmetrical peak corresponding to amorphous carbon and carbon nanofibres [6], set of Fe_3C peaks and some weak peaks of γ -Fe phase (Fig. 2c).

The Mossbauer spectroscopy has allowed to receive more detailed information about researched samples microstructure. The Mossbauer spectrum fitting of the initial catalyst sample is shown in Fig 3a. As this method is sensitive only to iron-containing-compounds we can not see in the spectrum a component corresponding pure oxide MgO. There is only one component in this spectrum - well resolved doublet with widened line widths ($\Gamma=0,64$ mm/s) and parameters characteristic for superparamagnetic MgFe_2O_4 ($Q=0,9$ mm/s and $\delta=0,31$ mm/s). At downturn of temperature up to 80 K, it is not revealed appearance of magnetic splitting in the spectrum (Fig. 4b). We can see only small temperature shift and spectral intensity increase in it. These facts testify that oxide superparamagnetic particles of the catalyst are in high dispersed condition, with the sizes $< 10\text{nm}$ [3].

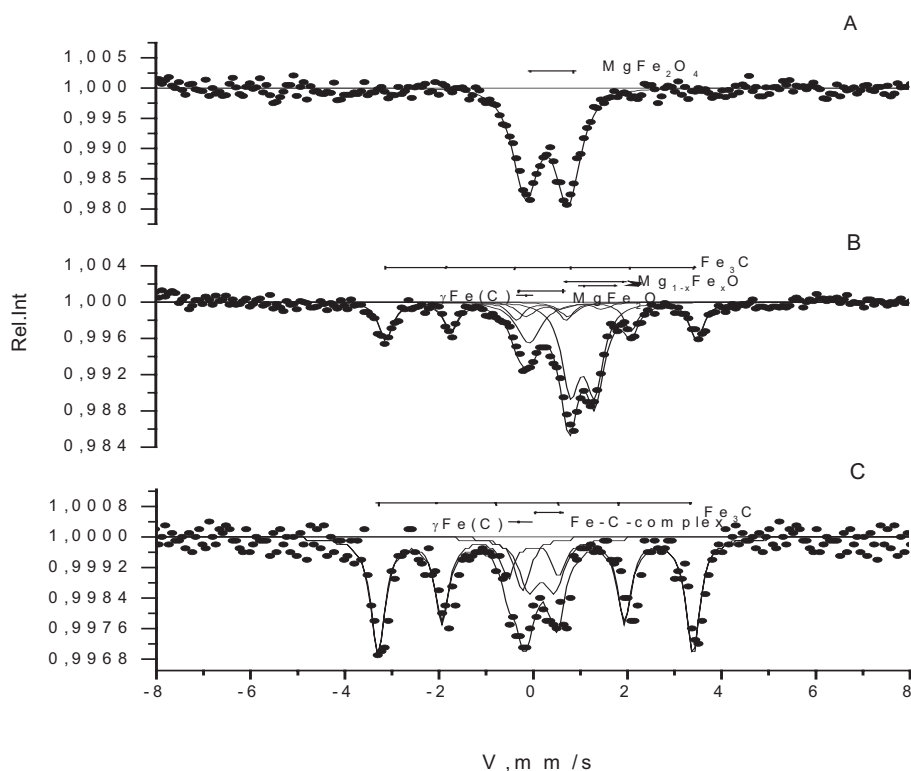


Figure 3. Mossbauer spectra of samples: 3a - initial catalyst, 3b - catalyst with formed on it carbon nanostructures, 3c – washed carbon nanostructures.

The changes in the Mossbauer spectrum of the sample 2 (Fig. 3b) demonstrate the structural and chemical transformations in the catalyst after the synthesis. The detailed mathematical analysis has allowed to resolve in it magnetic-splitter sextet with parameters characteristic for Fe_3C . This component occupies about 30 % of the whole spectral area. Besides that this spectrum contains also a doublet

($Q=0,9$ mm/s and $\delta=0,32$ mm/s) which corresponds to MgFe_2O_4 and is responsible for the rests of the initial catalyst. It takes in a spectrum approximately 7% from the common area. This essential reduction of a doublet area in comparison with a spectrum of the initial catalyst allows to conclude that during the synthesis MgFe_2O_4 undergoes complex structural and chemical transformations leading to Fe_3C , and carbon nanotube and nanofibres formation. Also in examined spectrum there are two doublet subspectra which spectral parameters analysis allows to attribute them to two Fe^{2+} nonequivalent positions in formed $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ solid solution. The intensities ratio of these two doublets in Mossbauer spectrum allows to find the amount of the iron content in solid solution as $x=0.15$ [4]. Central singlet (with $\delta = 0,07$ mm/s) corresponds to $\gamma\text{-Fe}$ (C) with concentration of carbon in a sample about 1,5 % [5].

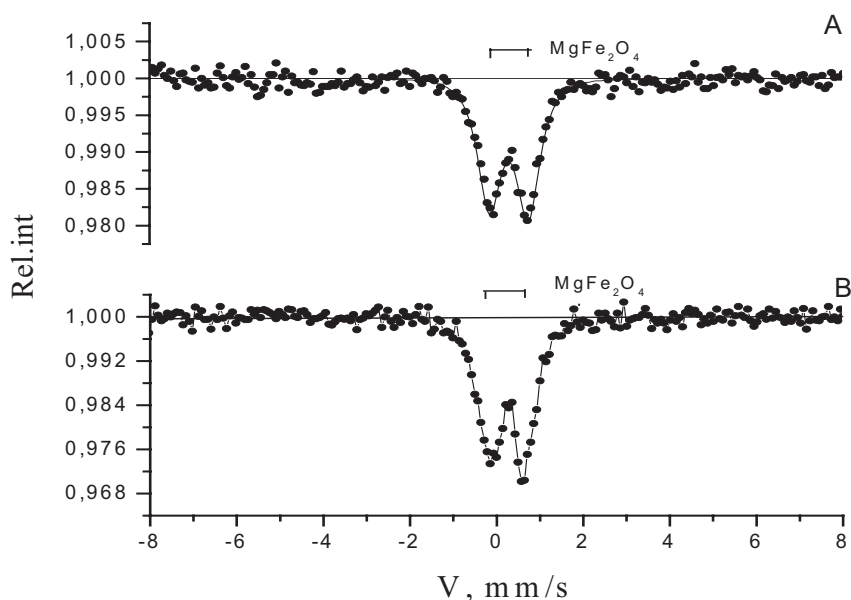


Figure 4. Mossbauer spectra of initial catalyst obtained at 300 K (a) and at 80 K (b).

Mossbauer spectrum of a sample 3 (products of the synthesis cleaned from the catalyst) is shown in Fig. 3 c. It has a worse quality in comparison with Fig. 3 a-b spectra because of very small iron content. The fitting of this spectrum allowed to allocate 3 subspectra: the doublet corresponding to Fe_3C (about 77 % spectral area), weak singlet with parameters, characteristic for $\gamma\text{-Fe}$, and a doublet with parameters ($Q=0.55$ mm/s, $\delta=0.20$ mm/s). It is possible to assign this component to iron - magnesium -graphite complex. The similar complex, being a transitional stratum between a metal particle and a carbon nanotube, was determined by us at the researches of carbon nanotubes formation on iron - nickel catalyst in the process of arc-synthesis [7]. The difference between these two complexes is expressed in change of isomer shift parameter value due to a substitution nickel by magnesium in the used catalyst.

4. Conclusions

Our structural study have shown, that the prepared catalyst represents a mix of two connections: MgO ($d \sim 30\text{nm}$) and ultra disperse MgFe_2O_4 ($d \sim 10\text{nm}$).

During the synthesis, besides carbon nanofibers formation, a plenty of chemical transformations occurred in the catalyst: incorporation of ions Fe in MgO lattice and $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ solid solution formation as well as Fe_3C , $\gamma\text{-Fe}$ and iron-magnesium-graphite complex, being a transitional stratum between a metal particle and a carbon nanofibre formation. Were revealed inert ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$) and active, very fine particles of the catalyst (MgFe_2O_4) components which are involved in the process of carbon nanofibres formation.

Acknowledgments

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CARBON NANOMATERIALS ON THE BASE OF CATALYTIC HYDROCARBON PYROLYSIS: DEVELOPMENT AND PERSPECTIVE USE

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Abstract. At present stage of development of carbon nanomaterial production technologies the great attention is paid to the creation of the equipment which allow obtaining these materials in significant amounts.

Tambov State Technical University (TSTU) in cooperation with research and industrial teams carries out research, design and manufacturing works for process equipment to obtain carbon nanofibres and nanotubes.

As a result of this work the experimental industrial production technologies for hydrocarbon catalytic pyrolysis were developed.

Experimental samples of products (nanofibres) were obtained.

Keywords: carbon nanofibres, pyrolysis, x-ray diffraction, reaction kinetics

1. Introduction

The latest researches on carbon nanomaterials (CNM) application promote their actual industrial use.

CNM have many unique features: perfect strength in combination with high elastic deformation values, good electrical conduction and adsorbability, autoelectronic emission ability and gas accumulation.

These materials can be successfully applied as fillers for constructional materials and hydrogen accumulators, radioelectronics elements, lubricant additives, high effective adsorbents etc.

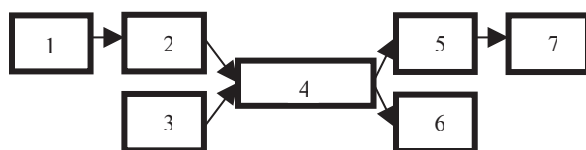
Considering possible significant consumption CNM industrial production becomes a pressing problem.

2. Experimental

“Tambov Innovative Technological Engineering Centre” in cooperation with Tambov State Technical University and “Artyomov Tambov Plant “Komsomolets” realizes the project of CNM industrial production.

At present research on obtaining technologies for these products by catalytic hydrocarbon pyrolysis was made in lab conditions. Main method advantages are following: pyrolysis process realizes in direct contact of catalyst and carbonaceous gas at rather low temperatures (600-800°C) and air pressure, opportunity for carbonaceous gas recycling, low initial reagent costs and wastes volume. CNM obtaining technology is flexible and can be used for synthesis of nanofibres and nanotubes, for nanomaterials with various morphological, physical and mechanical properties.

Principal diagram for technological production process is shown in Fig. 1.

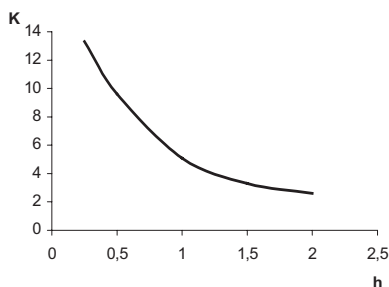


1-catalyst obtaining, 2- catalyst dosing and delivery; 3-hydrocarbon delivery; 4- carbon nanomaterial synthesis; 5-Product unloading; 6-Hydrogen and undecomposed hydrocarbon extraction; 7-Obtained nanomaterial purification of catalyst.

Figure 1. Diagram for CNM technological production process.

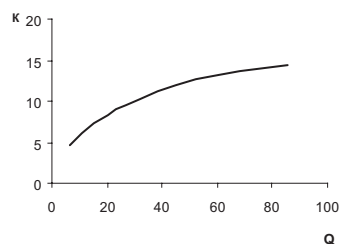
Hydrocarbon gas pyrolysis was made in the batch action reactor. Carbonaceous gas, to be more exact propane-butane mixture of various percentage ratio, was given to the surface of powdery catalyst, which was coated with thin even layer on the plate made of stainless steel. Experimental device for ultradispersed catalyst coating of the plate was developed and optimal hydrodynamic requirements against hydrocarbon delivery to reactor working area were investigated.

The results of experimental research on the product yield dependence on catalyst layer thickness h and gas rate value Q are shown in Figs. 2 and 3 correspondently. Obtained results allowed us to fix optimal charge parameters for pyrolysis in the interests of the efficiency.



K – specific product yield, g/g_{cat}, h – catalyst layer thickness, mm

Figure 2. Graph of dependence of specific product yield on catalyst layer thickness.

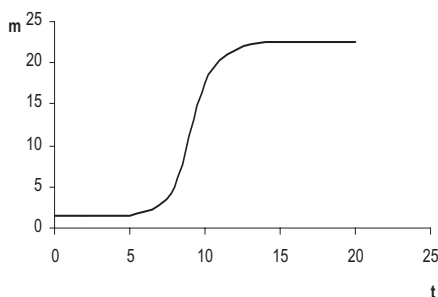


K – specific product yield, g/g_{cat}, Q – gas rate, l/hour

Figure 3. Graph of dependence of specific product yield on gas rate value.

The experiments with various stay time of catalyst in carbonaceous gas environment were carried out to reveal process kinetics and to determine reaction proceeding time.

The results of experiments are shown in Fig. 4.



m – weight of material obtained during the reaction, mg, t – process time, min

Figure 4. Graph of dependence of obtained material weight on pyrolysis time.

Specific yield was calculated as CNM obtained weight-to-catalyst weight ratio. The reactor with the vibrofluidized catalyst layer was considered as one of the versions for constructive pyrolysis design. Catalyst layer was placed to reactor body – cylindrical heating shell, and was converted into vibrofluidized condition, and gas was given through distribution device.

As a result of research we obtained kinetic dependences and charge features of the catalyst and reagents, that allowed us to make a pilot reactor for CNM obtaining in catalyst vibrofluidized layer.

The results of experimental research became the base for engineering recommendations for experimental industrial equipment, which is being produced at the moment. The expected efficiency of the equipment unit is 2000 kg/year with one-shift working mode.

On different stages of research our partners were scientists from several institutes of the Russian Academy of Science, in particular Ioffe Physical and Engineering Institute, Solid State Physics Institute and High-Molecular Compounds Institute. They helped us to make complex analysis of obtained CNM specimens by using modern measuring equipment.

Generalized results of the analysis made by different methods show that obtained CNM are filament nanocarbon fibres (CNM) with diameter from 8 to 100 nm, consisting of the polycrystalline nanographite entrained in amorphous carbon (Fig. 5).

On using various CNM purification methods (acid washing, ultrasonication, high temperature vacuum annealing) we managed to remove almost all the catalyst impurities and soot inclusions.

Qualitative analysis of purified CNM was made on the electron probe microanalyzer Camebax with the wide wavelength range (from 1 Å to 20 Å) with the use of the analyzer crystals PET, TAP and LIF (Fig. 6). The x-ray diffraction research was made on the diffractometer “Geigerflex” with radiation $\lambda=1.789$ Å and with a step 0,01 grad (Fig. 7).

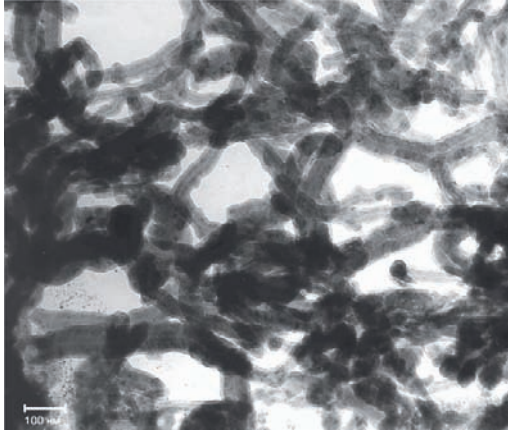


Figure 5. CNM microstructure photo.

This analysis confirmed the high purity of product and almost uniform distribution of residual impurity (Ni, Mg) amount in CNM.

There was fixed: density $\sim 2,2 \text{ g/cm}^3$, pore surface square $\sim 150\text{-}180 \text{ m}^2/\text{g}$, pore radius 30-50 Å, elasticity modulus 300-320 MPa and other physical and mechanical features.

The results of measurement of convertible sorption hydrogen capacity by volumetric method in almost real production conditions ($t = 20^\circ\text{C}$, $P_{\text{H}_2} = 13,5 \text{ MPa}$,

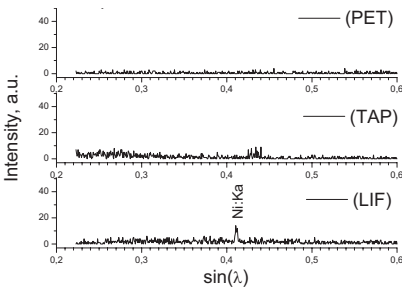


Figure 6. Qualitative analysis of purified CNM.

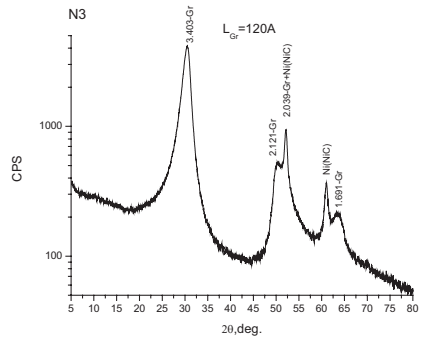


Figure 7. X-ray diffraction research.

desorption at $<300^\circ\text{C}$) are of great interest for practical application of CNM. This parameter was equal to 4,8wt.%; in measuring accuracy limits that corresponds to minimal CNM requirements ($\pm 0,7\%$), for commercial systems of accumulation and storage of hydrogen.

CNM capability for hydrogen accumulation may be increased by selection of appropriate catalyst (e.g. on the base of La), by magnifying of its dispergation level, by variation of carbonaceous raw components and pyrolysis mode.

The research on the efficiency of CNM use as a filler of polymer matrix of polyamide-6 applying now in polymer material technology is carried out together with the scientists from Voronezh State Technical University.

It is known, that physical and mechanical properties of carbonic composites on the base of this polymer (UPA 6-15, ..., UPA 6-40), where carbon fibrous materials "Ural" and "Viskum" are applied as a filler, depend on its weight fraction and uniformity of the filler distribution in the composite.

CNM obtained by pyrolysis with diameter 40-80 nm and length to 1 micrometer have elasticity module greater in more than 3 times, than that applied in UPA. Considering CNF nanosize, their capability for uniform distribution in polymer matrix we should achieve higher physical and mechanical features of the composite at lower volume content of the carbon filler.

The application field of this new material includes first of all the articles for antifrictional and constructional purpose.

The research of the CNM use opportunities as carbon electrodes for lithium batteries, gas-distribution layers of fuel cells, adsorbents and filters was carried out in Ioffe Physics Engineering Institute.

At present the preliminary results in the efficiency of high-dispersed CNF application as additives (to 0,5 wt.%) to the doped and undoped oils, and also the creation of composite materials with radar absorbent properties were obtained.

The CNF market formation in the Russian Federation may make a contribution to the wide application of these advanced materials in many branches of science.

The authors are extremely interested in cooperation in the CNF promotion into economy and are ready to give the material for its application research.

3. Conclusions

The industrial technology for the CNMs obtaining was developed. The complex analysis of the obtained samples was carried out; the ways for the further CNMs application were demonstrated.

SOLUTIONS OF POLYSTYRENE AS A CARBONIZATION PRECURSOR FOR THE MATRYX SYNTHESIS OF CARBON NANOSTRUCTURES

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Abstract. Carbon nanostructures were prepared by the carbonization of polystyrene, which was introduced as solutions into fumed silica based composites-matrices. Composite-matrices were impregnated with polystyrene solutions, or the latter were used as a dispersion medium at the stage of forming the composite-matrix. The precursor was carbonized at 750 °C in an argon stream. It has been found that the structure of the carbon formed depends both on the method of introducing the precursor into the composite-matrix and on the conformation of polystyrene macromolecules in the solution. When impregnating with polystyrene solutions, carbon tubes of different diameter (of up to 320 nm) or aggregates of up to 100 nm particles are formed in composite pores after carbonization. When polystyrene solutions are used as a dispersion medium, carbon structures in the form of segmented spheres (60 nm), “shells” (up to 100 nm in diameter) and aggregates of up to 100 nm particles are formed after polystyrene carbonization. The composition of the carbon formed was determined by XPS.

Keywords: fumed silica, carbon precursor, polystyrene, carbonization, carbon nanoparticles

1. Introduction

Modification of porous inorganic materials by carbon makes it possible to obtain porous carboniferous composites with high thermal and chemical stability and strength. To introduce carbon into pores, both gas phase pyrolysis and carbonization through thermochemical solid-phase reactions are employed. The formation of carbon structures depends on carbonization conditions: process rate, precursor concentration, presence of catalyst, etc. [1-3]. Phenolic resins, polyimides, carbohydrates, condensed aromatic compounds are most widely used as polymeric and organic precursors[4-6].

When polymers are used as precursors, they are generally applied as a thin film to a porous matrix. After carbonization, the polymer film changes into a carbon coating. The use of matrices with definite structure opens new possibilities for obtaining nanostructured carbon surface layers on an inorganic matrix.

The aim of this work was to study the effect of solutions of polystyrene as a precursor on the fabrication, by carbonization, of carbon nanostructures in fine silica based composites-matrices.

2. Materials and methods

The carbonization precursor was polystyrene (PS) with a molecular mass of 240000. To introduce PS into composites, its solutions in ethyl acetate with a concentration (C) of 0.25, 1.5 and 5.0 g/100 mL were used.

The precursor was carbonized at 750 °C in an argon stream during 30 min.

The structure-forming agent for the fabrication of composites-matrices was fine nonporous silica – aerosil (mean particle size, 80 nm; $S_{sp}=50$ g/m²). To 1g of aerosil was added 4mL of dispersion medium (ethanol-water mixture, ethyl acetate or polystyrene solutions). Silica nanoparticles form stable spatial structures, gels, owing to their ability to self-assemble into ordered structures in a liquid dispersion medium[7-9]. Gels were dried at room temperature to constant weight. The composite obtained after drying gel is a porous material with a system of open pores. The total porosity of composites was determined by impregnation with carbon tetrachloride [7].

A composite obtained from aerosil and an ethanol-water (2:1) mixture with a total porosity of 65% was used as the matrix to be impregnated with polystyrene solutions. The impregnation time was 7 and 24 h.

To etch away silica, carbonization product samples were treated with a mixture of concentrated sulfuric and hydrofluoric acids (5 drops of H₂SO₄ and 1 mL of HF), boiled dry and washed with water. From the precipitate obtained were prepared dispersions in acetone, which were used to determine the size and shape of particles on a JEM100CX-II transmission electron microscope by a commonly used procedure[10].

X-ray photoelectron spectra were obtained on a Kratos Analytical «SERIES 800 XPS» electron spectrometer using a nonmonochromatic MgK_α X-ray source (hν=1253 eV). During the experiment, vacuum in the analytical chamber was 5·10⁻⁹ Torr. The energy resolution, which is defined as Ag3d_{5/2} line half-width, was 1.1 eV. The accuracy of binding energy determination was ≤0.1 eV. The electron binding energy E_b was calibrated against the standard C1s line of carbon electrons on the surface of samples under investigation(284.5 eV). Samples in the form of powder were applied to an adhesive tape.

3. Results and Discussion

It is known [11] that in polymer solutions there is an equilibrium between associated and solitary macromolecules. Dilute solution consists of individual macromolecules, between which there is practically no intermolecular interaction. Increasing the polymer concentration leads to an increase in the size of the aggregates of macromolecules and in their number in unit volume. In concentrated

polymer solutions, the size of the aggregates decreases and approaches the size of undisturbed macromolecules.

Polystyrene (PS) is the simplest carbon-chain polymer, which contains a phenyl ring. This polymer contains no heteroatoms and is readily soluble in most organic solvents; this makes it possible to use its solutions to assess the effect of the spatial organization of macromolecules (conformation) on the microstructure of the carbon obtained, for it is known that the change in fumed carbon structure may be caused by a difference in the supramolecular structure of carbonization precursors [12]. According to Ref.[13], the mean size of aggregates for solutions of PS in ethyl acetate with a concentration of 0.25 g/100 mL is 1000 Å; at 1.5g/100 mL concentration, it is 4000 Å, and for 5.0 g/100 mL it is 890 Å, their number ($N \cdot 10^{-9}/\text{sm}^{-3}$) being 0.017, 0.27 and 6.88 respectively.

3.1. SYNTHESIS OF CARBON NANOSTRUCTURES USING POLYSTYRENE SOLUTIONS AS A DISPERSION MEDIUM

When the composite-matrix is formed with a polystyrene solution as a dispersion medium, the self-assembly of silica particles is influenced by the adsorption of macromolecules on their surface. During adsorption, both solitary macromolecules and their aggregates transfer simultaneously onto the adsorbent surface. Depending on solution concentration, not only the conformation of adsorbed molecules but also the number and size of macromolecular aggregates in the solution change on adsorption. This leads to the formation of complex-shaped structures, which are linked by a system of nonvalent interactions and consist of polymeric-inorganic blocks[8,14]; this is of interest in the preparation of a nanostructured medium (polystyrene-silica gel) as a precomposite for the fabrication of carbon structures in a matrix of silica particles.

According to [15], the adsorption of PS on aerosil surface OH groups involves participation of benzene ring π electrons. Only each third aromatic ring undergoes interactions with the silica surface, therefore the adsorption layer has a bulk structure. 0.95mg/m² of polystyrene is required for the formation of a monolayer on the surface of SiO₂ particles [15]. For the PS concentrations used in the present work, this corresponds approximately to C=1.5 g/100 mL, whereas the PS concentration of C=5,0 g/100 mL corresponds to about fourfold excess of polymer, and the PS concentration of C=0.25 g/100 mL is insufficient for the formation of a monolayer on the surface of SiO₂ particles.

Figure 1(a) shows a micrograph of a composite prepared by its carbonization with a polystyrene solution (C=5,0 g/100 mL). The total porosity of the composite was 39%, whereas the total porosity of silica-ethyl acetate composite was 68%. The concentration of macromolecules in this solution is sufficient for the complete coverage of the surface of SiO₂ particles with a polymer layer [15]. The adsorbed macromolecules are forced, because of steric effects, to retain the conformation they had in the solution, i.e. the adsorption layer is a bulk structure consisting of PS aggregates linked to one another[14]. It has been found by TEM that the carbon particles are segmented spherical features of up to 60 nm size (Fig. 1(b)). Small fragments, which seem to be fragments of larger structures, and conical and ovoid particles are also present.

At a PS concentration of $C=1.5$ g/100 mL, the aggregates of macromolecules are of the largest size, and a gel structure is formed in adsorption layers on their adsorption on the SiO_2 surface [14-16]. Besides, adsorption of individual polymer macromolecules takes place. From the micrograph of carbon structures obtained by the carbonization of such composites, which is shown in Fig. 1(c), it is seen that they are thin “shells” of up to 100 nm size. From unaggregated PS macromolecules, adsorbed on the surface of aggregates and individual SiO_2 particles, are formed aggregates of up to 100 nm carbon particles and individual particles of the size corresponding to that of SiO_2 particles.

In the case of carbonization of composites prepared using PS solutions of 0.25 g/100 mL concentration, the polymer concentration is insufficient for the complete surface coverage of SiO_2 particles [15]. The size of the aggregates of macromolecules is large enough for them to be located on the surface of aggregated SiO_2 particles [8,13], but their concentration is too low for the formation of a definite adsorption layer structure. Figure 1(d) shows a micrograph of carbon structures obtained by the carbonization of such composites. It is seen from the figure that they are replicas of aggregated SiO_2 structures, aggregates of up to 100 nm particles.

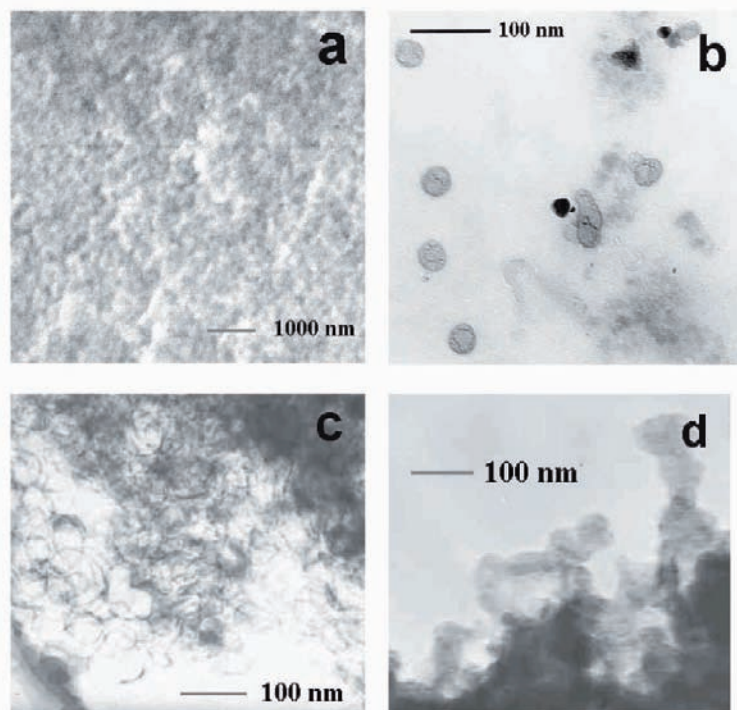


Figure 1(a). SEM image of a composite prepared by the carbonization of polystyrene introduced into the composite as a dispersion medium; (b,c,d): TEM image of carbon structures produced by the carbonization of polystyrene introduced into the composite as a dispersion medium. The PS concentration was 5.0 g/100 mL (a,b), 1.5 g/100 mL (c), 0.25 g/100 mL (d).

Thus, when PS solutions are used as a dispersion medium, the size of the carbon structures formed depends on polymer concentration: the lower it is, the more features corresponding to aggregates of SiO_2 particles. The fine structure of carbon features depends on the structure of PS adsorption layers and is determined by the supramolecular structure of the polymer solutions used.

3.2. SYNTHESIS OF CARBON NANOSTRUCTURES IN THE CASE OF USING POLYSTYRENE SOLUTIONS FOR THE IMPREGNATION OF MATRIX COMPOSITES

The use of PS solutions for the impregnation of composites showed that after carbonization, the samples that were impregnated with a solution with $C=5.0$ g/100 mL had a uniform black color throughout their volume. The composites impregnated with a PS solution with $C=0.25$ g/100 mL have some “blackness” gradient across sample thickness. For PS solutions with $C=1.5$ g/100 mL, the samples obtained remained practically white in the middle. These facts allow one to state that large aggregates of polystyrene macromolecules cannot penetrate the pore space of synthesized composites; they are adsorbed on the surface of pores and choke them, which prevents saturation of the pore space of composites by polymer.

Figure 2(a) shows a micrograph of carbon particles obtained by PS carbonization after impregnation of a composite with a PS solution with $C=5.0$ g/100 mL for 7 h. It is seen from the figure that the structures obtained are tubes 130–320 nm in thickness and several microns in length. The structure obtained of the carbon formed may be accounted for by the fact that on impregnation for 7 h, only the surface of pores in the composite-matrix is impregnated, which is apparently due to two causes. Firstly, when solutions of PS in ethyl acetate are used, silica surface OH groups form a hydrogen bond to solvent carbonyl groups, which hinders adsorption of polymer macromolecules [8]. Secondly, it was found in Ref. [16] that in the case of adsorption from concentrated polystyrene solutions, there is an induction period of 4–15 h, during which no increase in the amount of PS in adsorption layers takes place, and there is practically no adsorption.

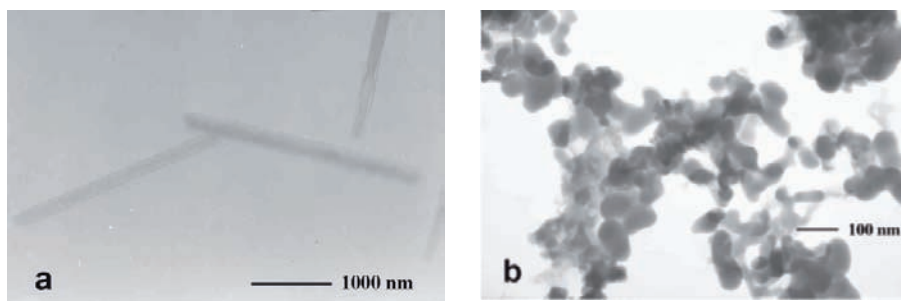


Figure 2. TEM image of carbon structures produced by the carbonization of polystyrene introduced into the composite by impregnation for 7 h(a) and 24 h(b). The PS concentration was 5.0 g/100 mL.

Increasing the impregnation time to 24 h leads not only to adsorption of PS macromolecules on pore walls but also to their penetration between composite-matrix structure elements (peptization) [8]. Though no changes in the composite-matrix were observed visually during impregnation, destruction of large aggregates of

silica particles and adsorption of macromolecules on smaller aggregates and individual SiO_2 particles seem to take place. The carbon structures obtained in such composites are agglomerates of up to 100 nm particles (Fig. 2(b)). The total porosity of the composite decreased to 59% after carbonization.

3.3. INVESTIGATION OF THE COMPOSITION OF CARBON COATING BY XPS

The X-ray photoelectron spectra of composites were recorded in the binding energy range of C1s and O1s electrons. In measured C1s curves, an asymmetry and noticeable broadening of lines are observed. This indicates the spectra to be complex and to consist of several components[17]. To establish individual components, the curve synthesis method was employed. The experimental curve was artificially reconstructed using increasing number of individual peaks. The lines due to carbon ($284.5 \pm 0.1 \text{ eV}$) and hydrocarbon groups (284.5 eV) were fixed. It appears to be not possible to establish definitely the presence of hydrocarbon groups in samples because of the presence of high-vacuum oil vapor in the instrument. The results of separation are shown in Fig. 3.

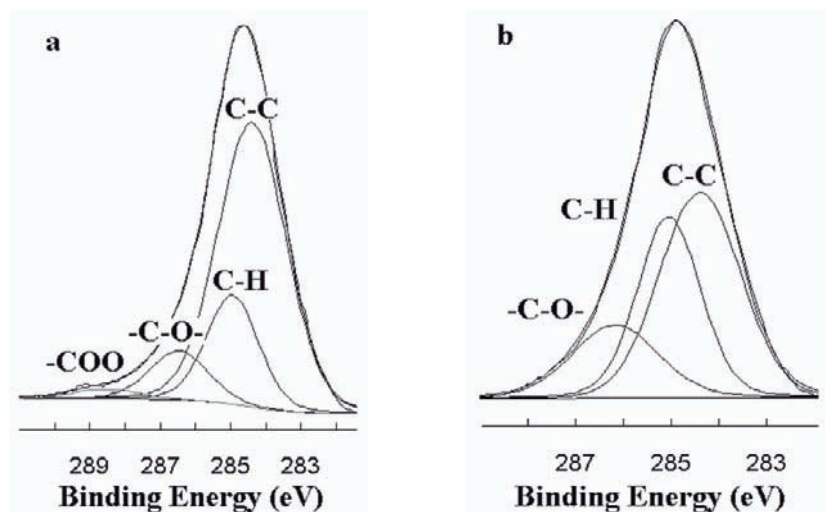


Figure 3. C1s spectra of carboniferous composites, into which polystyrene was introduced by impregnation (a) and together with dispersion medium (b). The PS concentration was 5.0 g/100 mL.

For the samples into which PS ($C=1.5 \text{ g}/100 \text{ mL}$) was introduced together with the dispersion medium, the C1s curve is asymmetric and consists of several components: peaks at 284.5 eV (C-C), 285.0 eV (C-H) and 286.1 eV (-C-O). Concentration in atomic %: C, 14.4; O, 57.5; Si, 28.1. For the PS concentration of 5.0 g/100 mL, peaks at 284.4 eV (C-C), 285.0 eV (C-H) and 286.1 eV (-C-O) are observed (Fig. 3(a)). Concentration in atomic %: C, 18.4; O, 56.0; Si, 25.6.

For the samples into which PS ($C=5.0 \text{ g}/100 \text{ mL}$) was introduced by impregnation (Fig. 3(b)), the C1s curve is asymmetric and consists of several

components: peaks at 284.5 eV (C-C), 285.0 eV (C-H), 286.5 eV (-C-O) and 288.5 eV (-COO). Concentration in atomic %: C, 20.6; O, 54.2; Si, 25.2.

The presence of Si1s curve indicates that during the preparation of samples for recording XPS's, fractures of the composite silica skeleton appeared, which have no carbon coating, and that the carbon coating is not homogeneous.

4. Conclusions

It has been found experimentally that polystyrene solutions promise much as carbonization precursors for the synthesis of carbon nanostructures in porous composites-matrices. Using polystyrene solutions, one can control the size and shape of the carbon structures formed by changing the conformation of PS macromolecules and interaction with composite-matrix structure elements:

- (1) When polystyrene solutions are used as a dispersion medium, the carbon structures formed are aggregates of up to 100 nm particles (PS concentration 0.25 g/100 mL), thin "shells" (PS concentration 1.5 g/100 mL), and segmented spheres of up to 60 nm size (PS concentration 5.0 g/100 mL).
- (2) When using polystyrene solutions for the impregnation of the composite-matrix, one must use concentrated solutions (PS concentration 5.0 g/100 mL), from which aggregates of macromolecules can penetrate into the composite pore space. After carbonization, carbon structures were obtained, which were tubes of up to 320 nm diameter or aggregates of up to 100 nm particles.
- (3) The carbon coating of the fine-silica skeleton of composites is not homogeneous and contains oxygenated surface carbon groups: (-COO, -C-O-) in the case of introduction of polystyrene by impregnation and (-C-O-) in the case of using polystyrene solutions as a dispersion medium.

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NANOCARBON MATERIALS

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Abstract. Nanocarbon materials and method of their production, developed by TMSpetsmash Ltd. (Kyiv, Ukraine), are reviewed. Multiwall carbon nanotubes with surface area 200-500 m²/g are produced in industrial scale with use of CVD method. Ethylene is used as a source of carbon and Fe-Mo-Al- mixed oxides as catalysts. Fumed silica is used as a pseudo-liquid diluent in order to decrease aggregation of nanotubes and bulk density of the products. Porous carbon nanofibers with surface area near 300-500 m²/g are produced from acetylene with use of (Fe, Co, Sn)/C/Al₂O₃-SiO₂ catalysts prepared mechanochemically. High surface area microporous nanocarbon materials were prepared by activation of carbon nanofibers. Effective surface area of these nanomaterials reaches 4000-6000 m²/g (by argon desorption method). Such materials are prospective for electrochemical applications. Methods of catalysts synthesis for CVD of nanocarbon materials and mechanisms of catalytic CVD are discussed.

Keywords: Carbon nanotubes, Carbon nanofibers, Chemical vapor deposition, Catalyst, Activation.

1. Introduction

Nanocarbons are among the most promising materials developed last years. Nanocarbon materials include fullerenes, carbon nanotubes (CNT), carbon nanofibers (CNF), nanodiamond, onions, and various hybrid forms and 3-dimensional structures based on these. Several years ago these materials were available in milligram-scale quantities. Now many of them are produced by tones per year. TMSpetsmash Ltd. research team has developed some new kinds of nanocarbon materials and processes for their production.

2. Experimental

For large scale production of carbon nanotubes and nanofibers chemical vapor deposition (CVD) method is most effective. Acetylene, ethylene, propylene, methane, natural gas (consisting predominantly of propane), carbon monoxide were used as a source of carbon [1-8] (in view of large number of publications on CNT synthesis these references are selected arbitrary). Ethylene and possibly propylene are most convenient carbon sources for mass synthesis of high quality multiwall CNT (MWNT).

No observable admixture of amorphous carbon was present in MWNT CVD-grown on catalysts containing particles of catalytically active metals on dispersed metal oxide supports such as silica or alumina [1, 9]. This simplifies purifying of the product and for many applications allows use of as-synthesized product without purification.

High quality MWNT were obtained from acetylene on $\text{Co}_3\text{O}_4/\text{MgO}$ catalyst [3]. However, commercial acetylene often contains impurities which sometimes have harmful influence on the process. For instance, we observed poisoning of a catalyst, probably by phosphine, when obtaining CNF from commercial acetylene on Fe/C/SiO_2 catalyst. After careful purifying of acetylene the process proceeded normally. Further, sometimes aromatic hydrocarbons form if the catalyst used is not sufficiently selective. In our experiments formation of aromatics was observed frequently in case of acetylene. This creates ecological problems.

From the reasons considered above we used ethylene as a source of carbon for growing of MWNT. With use of effective catalysts conversion of ethylene to carbon was high (90-100%) with minor amount of aromatics formed.

We have created pilot installation for CVD production of multiwall carbon nanotubes from ethylene in industrial scale. MWNT produced by this process have average diameter 12-20 nm, surface area near 200-500 m^2/g , mass content of minerals 6-20% for non-purified NT and <1% for purified NT. Electron images of MWNT samples with different surface area (200, 390, and 500 m^2/g) are shown in Figs. 1-3.

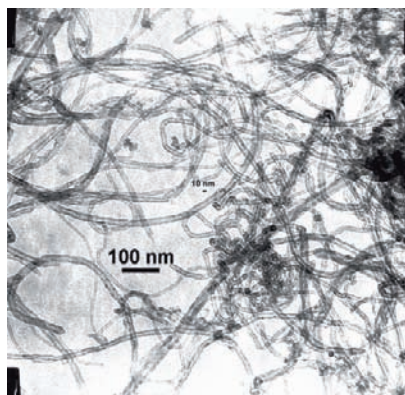


Figure 1. MWNT from ethylene, surface area 200 m^2/g .

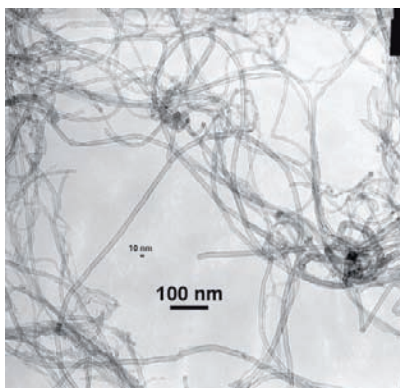


Figure 2. MWNT from ethylene, surface area 390 m^2/g .

As is known, surface area of carbon nanotubes, with some assumptions, interrelates with its diameter and number of walls [10]. Taking into account these data, one can estimate average number of walls to be 2.8 at CNT diameter near 10 nm and surface area 500 m^2/g . These parameters are close to reported for double-wall CNT samples containing 50% DWNT produced by Shenzhen NTP (China).

MWNT are produced in form of black powder with bulk density of 15-40 g/dm^3 . Experiments carried out by us have shown that low bulk density MWNT samples are preferable for application in composite materials, particularly for PTFE-MWNT composites. So, we tried to produce MWNT with the bulk density as low as possible. This was achieved by use of co-precipitated $\text{Fe}_2\text{O}_3\text{MoO}_3\text{-Al}_2\text{O}_3$ catalysts containing aerosil (fumed silica) as a pseudo-liquid diluent of growing nanotubes [11, 12].

Usual device used for mass CVD production of carbon nanotubes is a fluidized-bed reactor [7]. In our laboratory installation we successfully used rotating reactor

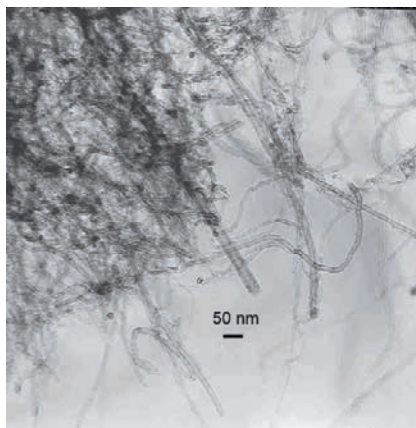


Figure 3. MWNT from ethylene, surface area $500 \text{ m}^2/\text{g}$.

[11, 12]. In rotating reactor the reaction mass fluidization state is independent on gas flow. This allows to adjust gas flows according to activity of a catalyst regardless to fluidization regime.

For different electrochemical applications such as batteries, supercapacitors, fuel elements porous carbon nanomaterials are used. We have obtained porous carbon nanofibers by CVD method from acetylene with use of new $(\text{Fe}, \text{Co}, \text{Sn})/\text{C}/\text{Al}_2\text{O}_3\text{-SiO}_2$ catalysts prepared by mechanochemical method [13, 14]. The porous nanostructures formed (Fig. 4) somewhat resembles structures, synthesized in [15] on titania-containing catalyst.

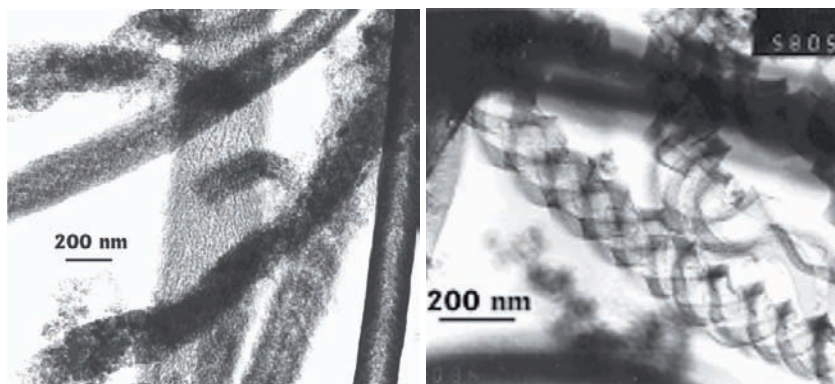


Figure 4. Porous carbon nanofibers grown from acetylene on $\text{Fe}/\text{C}/\text{SiO}_2$ catalyst.

In spite of high surface area (nearly $300\text{-}500 \text{ m}^2/\text{g}$), oxidation of the samples in air begins at temperatures higher than 500°C (Fig. 5). This indicates absence of “amorphous” carbon, which usually burns in air at $350\text{-}450^\circ\text{C}$. However, structure of the nanofibers obtained remains unclear.

XRD plots for these samples are shown in Fig. 6. For the sample 1 (obtained on catalyst $\text{Fe}/\text{C}/\text{Al}_2\text{O}_3\text{-SiO}_2$) two main maximums are observed with $2\theta=17,9^\circ$ and $25,9^\circ$. The last corresponds to interlayer distance $3.44 \text{ \AA}$ for packages of

orientationally-disordered graphene layers. The structure of phase corresponding to the first maximum (interplane distance 5.0 Å) is unclear. As is seen, the sample 2 (obtained on catalyst Fe-Sn/C/Al₂O₃-SiO₂) consists completely of this phase.

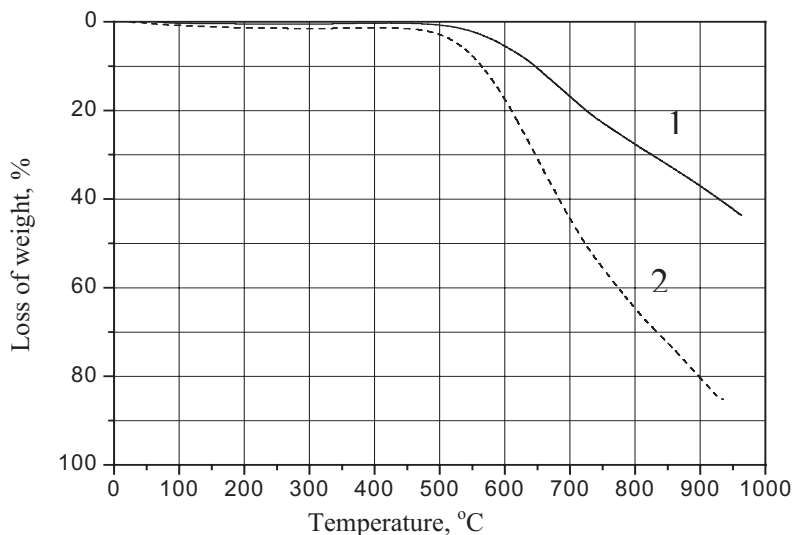


Figure 5. TG plot for samples of porous carbon nanofibers grown from acetylene on mechanochemically prepared catalysts:

1 – on catalyst Fe/C/Al₂O₃-SiO₂, surface area of CNF 335 m²/g;

2 – on catalyst Fe-Sn/C/Al₂O₃-SiO₂, surface area of CNF 475 m²/g.

Rise of temperature 10°C/min, in air.

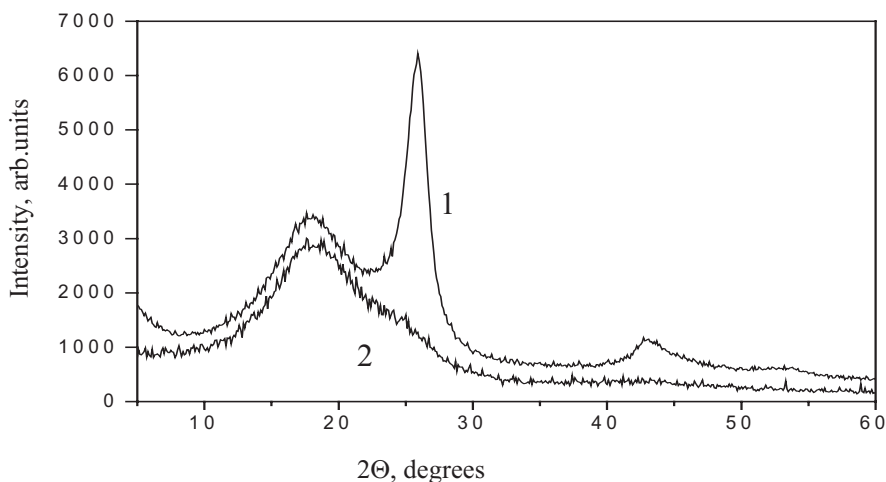


Figure 6. XRD plots for samples of porous carbon nanofibers grown from acetylene on mechanochemically prepared catalysts:

1 – on catalyst Fe/C/Al₂O₃-SiO₂;

2 – on catalyst Fe-Sn/C/Al₂O₃-SiO₂.

Radiation CuKα.

Surface area of as-obtained CNF is nearly 300-500 m²/g. One of the effective methods of activation of different carbon materials is treatment with melted KOH at 400-900°C. High surface area (up to nearly 3000 m²/g) carbon materials were obtained [16, 17]. This method was also applied to carbon nanotubes. Significant development of surface was observed, from 465 m²/g for starting MWNT to 1184 m²/g after activation [18]. Also, KOH activation of carbon nanofibers resulted in increase of surface area from initial 174 m²/g up to 1212 m²/g [19]. When activated our nanofibers, we obtained for some samples very high effective surface area, nearly 2000-4000 m²/g and in some experiments even 6000 m²/g (measured by argon desorption method). In electron image of activated material (Fig. 7) fiber-like structure is observed.

In spite of physical vagueness of such high surface area values these materials are interesting for electrochemical and hydrogen storing applications. One can suppose that slit-like pores exist in these materials. Activated CNF were investigated as a hydrogen adsorbing electrode materials instead of metal hydrides [20].

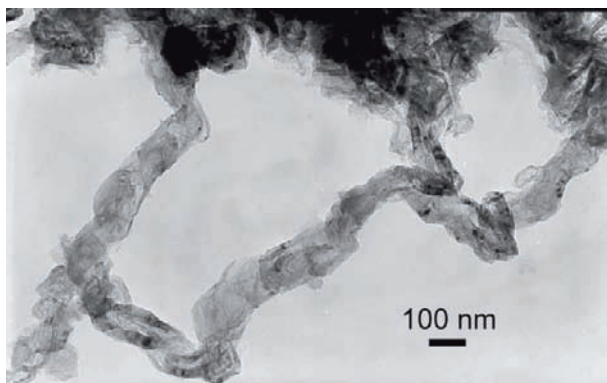


Figure 7. High surface area activated CNF (4000 m²/g).

Along with improving of CNT and CNF production technology new methods of nanocarbon materials obtaining are of interest besides of widely used arc-discharge and CVD techniques. One of promising ones is solid-state reaction method. We have investigated a new nanocarbon-producing system, CaC₂-S [21]. When reacted with sulfur vapor at 400-600°C or in burning mode, calcium carbide powder gives nanotubes together with other carbon nanoparticles (Fig. 8):



This reaction gives high yield of carbon (44-80%) and can be easily scaled. Purifying of the raw material includes treatment of it with sodium carbonate solution with following treatment with acid. Surface area of nanocarbons obtained was 64-500 m²/g, specific electric resistance of powder 0.02-0.07 Ohm.cm.

As is known structure and properties of CNT and CNF obtained by CVD method in great extent depends on catalyst used in this process. Even for catalysts of the same composition, for instance, well-known Fe₂O₃-MoO₃/Al₂O₃ system, properties and yield of nanocarbon materials strongly depends on the catalyst preparation method.

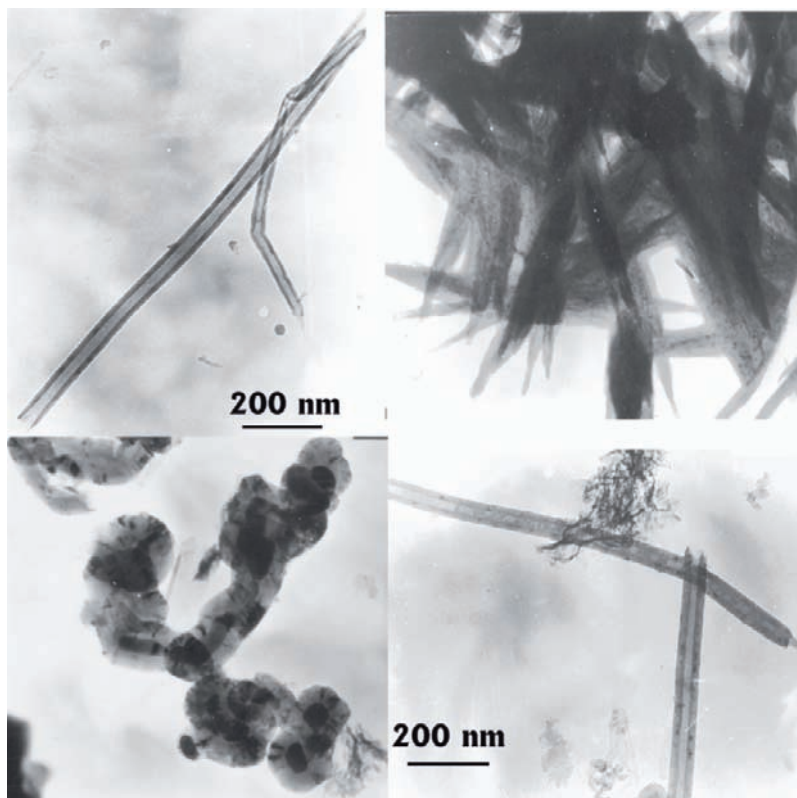


Figure 8. Carbon nanoparticles formed in the reaction $\text{CaC}_2 + \text{S}$.

We have investigated different methods of obtaining catalysts for CNT/CNF CVD production from ethylene and acetylene. These methods use co-precipitation, “appearing reagent”, redox, sol-gel and mechanochemical techniques. Good results were obtained with $\text{Fe}_2\text{O}_3\text{-MoO}_3/\text{Al}_2\text{O}_3$ co-precipitated with use of urea as a reagent slowly evolving ammonia. Both 2-valent [11, 12] and 3-valent iron salts can be used for co-precipitation. The catalysts so obtained are effective for CNT growth from ethylene. However these catalysts are much less effective for CNT/CNF growth from acetylene.

Highly effective iron-containing catalysts for synthesis of porous CNF from acetylene were obtained by mechanochemical method [13, 14]. It was found that carbonization of iron-containing organic precursors in oxygen-free atmosphere greatly increased catalytic activity in CNF growth process. On contrary, similar treatment of catalyst precursors greatly decreased catalytic activity in CNT growth process from ethylene. It may be that porous CNF growth process from acetylene is initiated by free-radical centers on carbon clusters adjacent to iron particles.

On the other hand, it is possible that CNT growth from ethylene is promoted by Lewis or Brønsted acid centers on $\text{MoO}_3/\text{Al}_2\text{O}_3$. The $\text{MoO}_3/\text{Al}_2\text{O}_3$ system is a typical solid acid like some other mixed metal oxides such as $\text{WO}_3/\text{Al}_2\text{O}_3$, WO_3/ZrO_2 , WO_3/TiO_2 , $\text{MoO}_3/\text{TiO}_2$ [see review articles 22-25]. Besides Lewis acid

centers, Broensted acid centers can appear in these systems after reduction with hydrogen. It is possible that the first step of the CNT growing process is chemisorption of ethylene molecules due to donor-acceptor interaction with Lewis acid centers or their protonation by Broensted acid centers. Carbenium ions formed diffuse to neighbouring clusters of iron where dehydrocyclization proceeds with formation of hemispherical graphene structure around the iron cluster. When the process continues, the hemisphere separates from iron cluster and nanotube begins grow. As our experiments showed, in case of "bad" catalysts, containing too much molybdenum oxide and little iron oxide (on alumina), ethylene converts to aromatic compounds, particularly, naphthalene, which form a dense smoke and crystals at the outlet of reactor. Thus, in absence of neighbouring iron clusters dehydrocyclization of ethylene to aromatic compounds proceeds, catalyzed by acid centers of $\text{MoO}_3/\text{Al}_2\text{O}_3$ system. How does iron promote formation of graphene structure, is an open question. Another question is whether formation of aromatics and graphene layers are competitive or consecutive processes. Taking into account that aromatic compounds, particularly benzene, demand higher temperature for obtaining nanocarbon than used in our experiments with ethylene (680-700°C), it seems more likely that the processes considered are competitive, but have common first steps – interaction of ethylene molecule with acid center and possibly initial stages of dehydropolymerization.

Continuing the analogy between transformations of hydrocarbons on superacid catalysts like $(\text{Pt})\text{WO}_x/\text{ZrO}_2$ at 200-400°C and formation of nanocarbon structures on $\text{Fe}_2\text{O}_3\text{-MoO}_3/\text{Al}_2\text{O}_3$ at 600-800°C, it should be mentioned that formation of carbon always occurs in the first process, but it is a harmful side-process which results in deactivation or catalyst. It is possible that at appropriate temperature typical solid acid catalysts (promoted by VIII Group metals) should be effective for obtaining nanocarbon materials.

3. Conclusions

The methods and installations are created which allow large-scale production of carbon nanomaterials with unique properties.

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THE PRODUCTION OF HYDRIDES IN TITANIC POWDERS UNDER DIFFERENT WAYS OF MANUFACTURING

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Abstract. Diffusion of gases in titanic powders depends on a way of manufacture, the conditions of lixiviation at hydrometallurgical processing of powders, and also on a condition and on the structure of the surface of particles. The different methods to investigate products of corrosion, as on a surface of particles, and in the fulfilled solutions in which the tests are performed, are given. The correlation between them is established. The influence of oxygen on formation of hydrides is shown. The recommendation for use titanic powders saturated by gas is given.

Keywords: titanic powders, diffusion of hydrogen and oxygen, oxides, hydrides in titanic powders, products of corrosion, structure of particles.

1. Introduction

The saturation by hydrogen always accompanies process of receiving the titanic sponge, and powders, as well as alloys on their basis. The non-ferrous metallurgy provides metal mainly with the content of hydrogen less than allowable concentration, at which the hydrogen fragility is possible. However, in the process of manufacturing the powders, and at technological operations during manufacturing of products, the increase of the content of hydrogen up to meanings appropriate to concentration limits of formation of titanium hydrides is possible [1]. During manufacturing the powders or manufacturing the products in such cases the development of hydrogen fragility is possible. Therefore, struggle with the saturating by hydrogen is one of the major problems in production of titanic powder products used in a space and aircrafts industry, mechanical engineering, rocket production.

At the same time, hydrogenation of titanium is widely used in industry; applications of titanium hydrides extend, and the ways of hydrogenation are being improved. Hydride of titanium is used, in particular, in nuclear engineering, in reactors of nuclear engines for the space equipment, electronics, cermet manufacturing, and power engineering. Hydride of titanium is an effective tool for biological protection against neutrons and rigid γ -rays. Last years the process of hydrogenation has been used as a productive way to crisp the titanium wastes of materials with the purpose to make them finer [2]. The growing interest to problems of hydrogenation in titanic powders in modern engineering leads to the necessity of careful study of all features of the given process.

In this connection an urgent problem in production of titanium sponge and powders is the all-round regular study of process of hydrogenation in powders of titanium, obtained in different ways.

2. Experimental

The saturation of hydrogen powders can occur at all stages of production, first of all at their hydrometallurgical processing, because particles adjoined with electrolyte and with a water solution of a hydrochloric acid, cooperate with atoms of hydrogen, chlorine, oxygen, hydroxide groups.

There is practically no free hydrogen in the environmental atmosphere. The main sources of the saturating by hydrogen in the process of producing the titanic powders are electrolyte, melt, water solutions of a hydrochloric acid at lixiviation. While interacting with titanium, hydroxide group (HE) is decomposed into oxygen and hydrogen, i.e. on the surface of particles there will be simultaneously both atoms of hydrogen, and atoms of oxygen, which begin to penetrate in the depths of metal.

Titanic powders obtained in different ways have structure α -Ti, which has two types of pores: octahedral and tetrahedral with the size of radius of an interstice equal to 0.62 nm and 0.34 nm, respectively. The speed of diffusion of atoms of implementation in titanium varies and also depends on the size of their radius of introduced elements, which are presented in Table 1. The atoms of these gases settle down in octahedral pores of a firm solution, instead of in tetrahedral, since they are larger in size. Octahedral pores are less rigid than tetrahedral, and are easily increased in size in the direction of the least diagonal octahedron [3]. The hydrogen, being in such emptiness, has large freedom of fluctuations of atoms, which increases the energy of the system as a whole, that thermodynamically it is not desirable. For this reason the solubility of hydrogen in α -phase is small.

TABLE 1. Speed of diffusion of atoms of implementation in titanium

The name of an element	Speed of diffusion, m/s $\cdot 10^{-15}$	The size of nuclear radius, m $\cdot 10^{-10}$
H	2,0	0,41
O	1,6	0,68
N	1,2	0,74
Cl	0,9	0,99

In VCK lattice β -modification of titanium of emptiness with radius 0,44 nm almost precisely correspond to nuclear radius of hydrogen 0,41 nm, and free fluctuations of atoms between knots do not occur. Hence, the system is more stable. Therefore, the hydrogen is well dissolved in β -phase (up to 2 %), stabilising it [3].

As it is shown in Table 1, the hydrogen has the highest speed of diffusion. The size of radius of its atom is $0,41 \cdot 10^{-10}$ m, and the size of octahedral pore in α -Ti is $0,62 \cdot 10^{-10}$ m, i.e. is 34 % less than the size of octahedral pore of a crystal lattice of titanium. Moving along octahedral pores, the hydrogen freely and quickly penetrates in the depth of a particle.

The oxygen also has high enough speed of diffusion $1,6 \cdot 10^{-10}$ m/s, but the size of its atomic radius is only 10 % more than the size of an octahedral pore α -Ti. Therefore, already at a room temperature the atom of the oxygen, which has got into an octahedral pore, stretches it, and its exit from the pore is difficult. Thus, formation of a monolayer of oxide film on a surface of a particle of a powder is possible, and its thickness changes with time.

From the literature it is known [1, 2, 4] that the stability in aggressive environment is naturally connected with the structure and condition of titanium. Therefore, performing the corrosion tests has allowed deeper understand a nature of gas saturation of titanic powders of different kinds of manufacturing, and to obtain new results.

Since titanium as a chemically active element can change valence from -2 up to +4 during lixiviation on the surface of a particle, there can be compounds of titanium with oxygen, nitrogen and hydrogen. Nevertheless, it has the large corrosion stability, due to formation on its surface of oxide, hydroxide film which reliably protecting from action of aggressive environments. The protective film consists of non metal compounds, has insufficient mechanical durability and easily collapses under pressure in places of sharp transitions of a relief of a surface of particles. The given circumstances also reduce protection properties of hydroxide films on the surface and cause high speed of corrosion of particles of titanic powders.

In Table 2 the data on entropy are presented, as well as data on enthalpy of compounds of titanium with a solution of an acid on a surface of a particle.

TABLE 2. Thermodynamic properties of connections of titanium with oxygen, nitrogen, hydrogen

Compound	Entropy, Dg/mol·deg	Enthalpy, kDg/mol	Fusion temperature, °C	Density, kg/m ³
Ti ₂ O	–	177,9	1540	4950
TiO	34,8	608-518,7	1750	4930
Ti ₂ O ₃	78,7	1627-1519	1900	4550
Ti ₃ O ₅	129,4	2457	2177	4570
TiO ₂	50,2	913,4-944	1850	4260
TiN	30,1	336	2950	4220
TiH ₂	62,6	29-31	650	4150

From Table 2 it is clear that hydride of titanium has low enthalpy, equal to 29-31 kDg/mol, and high entropy at formation and creation of the ordered system TiH₂. These are the lowest thermodynamic parameters in the process of creation of non metal connections of titanium among oxides and nitrides. The non metal layer, which is created on a surface consisting of oxides and hydrides, is fragile and exfoliates with time, forming a deposit in a solution (Table 3). This is confirmed by investigating the fulfilled solutions by methods of a nuclear magnetic resonance and chemical analysis, where valence of ions of titanium of an output in a solution was determined. The minimal content of ions of titanium in solutions is established by a method of the chemical analysis, corresponding to the cleanest purified powders. For the tests having the increased content of impurity (powders of a magnesium-reduced way of production), the process of dissolution of titanium proceeds less actively in comparison with electrolytic industrial powders, since they have a lot of oxygen and nitrogen, which deform and strengthen a crystal lattice of titanium.

TABLE 3. Output of titanium in solutions of a hydrochloric acid

Material	% HCl	Intensity Ti^{+3} , rel. units. (method ETMR)		Quantity Ti^{+3} in a solution, g/m ³ (chemical method)		The notes
		Time of endurance, h		Time of endurance, h		
		500	1000	500	1000	
Titanium powders of the increased cleanliness	5	1,00	8,75	17,89	21,23	Deposit Deposit
	10	3,70	18,20	36,46	40,17	
	20	10,00	69,10	49,62	44,05	
	30	13,20	115,00	65,66	47,81	
Electrolytic titanium powders of industrial production	5	1,30	4,15	27,86	23,71	Deposit Deposit
	10	9,35	14,00	36,19	24,40	
	20	33,00	53,60	78,39	45,43	
	30	34,70	110,00	47,99	43,65	
Titanium powders of a magnesium-reduced way production	5	3,84	6,30	31,12	19,34	Deposit Deposit
	10	19,10	15,70	37,83	29,76	
	20	40,10	128,00	76,13	44,84	
	30	39,00	115,00	54,11	39,88	

Depending on concentration of a hydrochloric acid during lixiviation of powders the process of saturation by gas develops ambiguously: it has a sine wave character. The established dependence of an output in a solution of ions trivalent titanium on the concentration of a solution according to data, obtained by the method of electronic paramagnetic resonance, has shown that at small time of exposure (50-100 hrs) the output of ions of titanium in a solution proceeds with the increasing speed. The pure powders react with environment less actively, polluted - more intensively. The speed of saturation of powders by gas at corrosion in solutions of a hydrochloric acid is increased with growth of concentration, and then is sharply reduced.

By X-ray phases research on equipment ДРОН-2 of powders of various hardness and different way of manufacture, it is established that during the first hours the oxide Ti_2O is formed (Table 4), since it has the greatest energy of inter nuclear connection, an its enthalpy is 177,9 kDg/mol. With the time of

TABLE 4. Phase structure of titanic electrolytic powders after corrosion in 5 % a solution HCl (the X-ray phases analysis)

Material	Test	Phase structure	
		500 h	1000 h
Titanium powders of the increased cleanliness	Powder Deposit	TiO , TiO_2 , TiH -	TiO , TiO_2 , TiH -
Electrolytic titanium powders of industrial production	Powder Deposit	TiO , TiH , α - Ti TiO_2 , $TiCl_3$	TiO_2 , TiH -
Titanium powders of magnesium-reduced way production	Powder Deposi	TiO , TiH , α - Ti TiO_2 , $TiCl_3$	TiO , TiH -

exposure in a solution of a hydrochloric acid the valence of titanium varies from -2 up to +4, and thus its enthalpy increases up to 944 kDg/mol (TiO_2).

It is clear from Table 4 that titanium oxide TiO_2 is formed and at longer exposures (500 and 1000 hrs), that is confirmed by metallographic research of a surface of powders.

On a surface of particles layers of hydrides and oxyhydrides of titanium were formed, crumbled, collapsed, exfoliated and again formed (Fig. 1). Layers had non-uniform thickness. The thickness of them on occasions reached 35-40 mk.

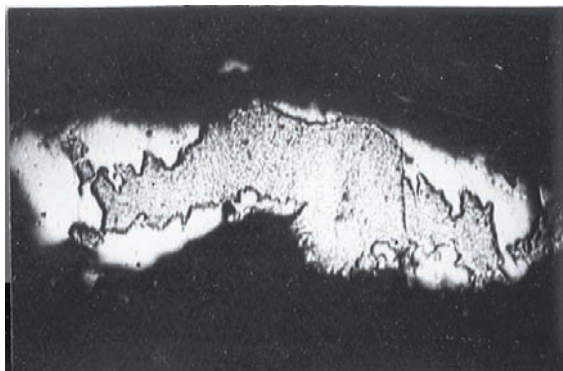


Figure 1. Formation of oxyhydride film on particles of titanic powders, x300.

Therefore, the hydrogen could diffuse in depth of a particle only overcoming a monolayer of titanium oxide Ti_2O . The oxide film sharply slowed down the diffusion of hydrogen. The process of diffusion of hydrogen and oxygen in depth of particles proceeds along borders of grains, line of sliding and twinning. Hydrides of titanium were formed on them (Fig. 2), decorating the structure of α -plates. Oxygen having high speed of diffusion as well tends to diffuse from the surface into the depth of a particle, forming thus enriched by oxygen alpha layer (Fig. 3).

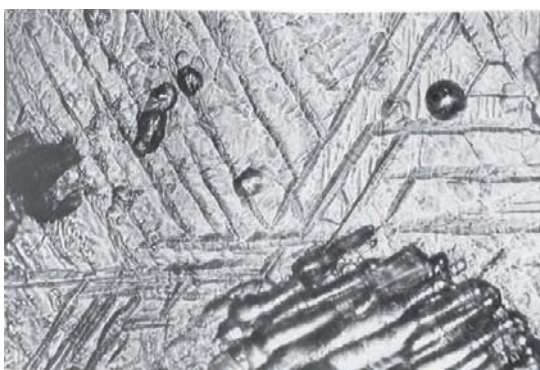


Figure 2. Structure of a surface particles of titanic powders saturated by gas, x300.



Figure 3. Structure in section of particles of powders, saturated by hydrogen, x300.

It is established that superficial alpha layer does not contain hydrides, they occur in structure of metal on some distance from a surface, the sizes of needles of these hydrides depend on time of exposure and concentration of a solution of electrolyte. Hydride needles are placed in all volume of a particle under an angle 60 and 120 degrees to each other. Therefore, on solubility of hydrogen in powders render appreciable influence not only structure and thin structure, but also contents of oxygen.

The structure of the pure and polluted powders also had specific features: the pure powders had hydrides of allocation in the form of plates or thick needles, which with increase of time of exposure in solutions of a hydrochloric acid were becoming more thin, and crumbled. In these needles there were strips of sliding and twinning (Fig. 4).

With the increase of hardness of titanic powder the similar processes accelerate, and after 100 hrs of exposure hydrides of titanium occur along the strictly parallel strips of sliding, which also have the certain strict crystal orientation under an angle 120 and 60 degrees.

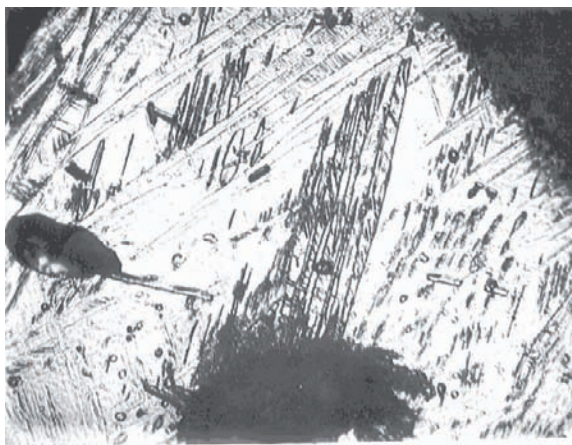


Figure 4. Features of formation and allocation of hydrides in powders of the increased purity, x300.

With the increase of concentration of a solution and hardness of powders occurred thinning and crushing of hydride needles, the randomness of their arrangement grows.

As the computer process of the statistical data has shown, there is a direct correlation between the contents of hydrogen and oxygen. The concentration of hydrogen increases with increase of the content of impurity in powders and change of a way of manufacture (Fig. 5).

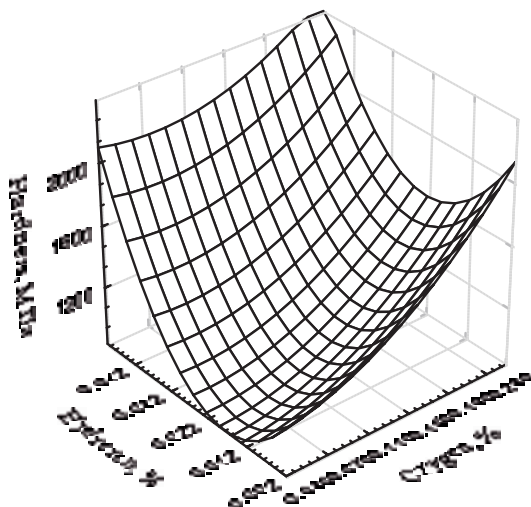


Figure 5. Mutual influence of oxygen and hydrogen on hardness of electrolytic titanic powders.

3. Conclusions

By results of the carried out research it is possible to conclude:

- properties of titanic powders essentially depend on the content of gas impurity in powders;
- there is an interrelation between the contents of hydrogen and oxygen;
- structure, mechanism of growth, morphology of hydride formations depend on the way of manufacturing of titanic powders;
- titanic powders obtained by electrolytic purifying have appeared to be the most stable.

Practically all titanic powders with a different degree of impurity can be recommended as a filling compound for corrosion resistant materials which work in muriatic environments.

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ELECTROCHEMICAL PROPERTIES OF NANODISPERSED DIAMOND

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Abstract. The object of this work was to investigate hydrogen oxidation and oxygen reduction from surface of modified nanodispersed diamond. The catalytic reactions on the surface of nanodispersed diamond have been studied after different treatment using heat-treated and electrochemical methods.

For developing the modifying of nanodispersed diamond there have been proposed the following treatment:

- special heat-treated treatment in hydrogen environment;
- (hydrogen electrode);
- precipitation of palladium (oxygen electrode).

It has been established that special heat-treated treatment to surface of nanodispersed diamond effective for hydrogen electrode material creation.

Precipitation of palladium of nanodispersed diamond surface it to be saturated with atomic oxygen. The quantity of atomic oxygen is higher than that of molecular oxygen.

It has been shown that nanodispersed diamond. after precipitation of palladium are effective catalyst of oxygen reduction.

Keywords: Hydrogen oxidation, oxygen reduction, nanodispersed diamond, surface, heat-treated treatment, hydrogen electrode, oxygen electrode.

1. Introduction

For many years the studies of surface modifications of synthetic diamond nanopowders have been conducted at the Institute for Superhard Materials. Our findings show that highly dispersed modified diamond powders hold a considerable promise in applications as adsorbents and catalysts of the oxidation and electrochemical catalysis [1-4]. This promise is based on the following special features of the material:

- morphological and microstructural stabilities;
- high degree of the specific surface development;
- possibility of a chemical modification of the surface;
- high corrosion stability in aggressive media and against polarization;
- low stable background current;
- possibility of the surface regeneration.

The aim of the present work has been to study catalytic properties of detonation-synthesized diamond nanopowders and to extend their applications. The catalytic activity of diamond was studied in reactions electrochemical catalysis.

The study of electrochemical catalysis implied the reaction of electrooxidation of hydrogen and electroreduction of oxygen into the diamond surface.

2. Experimental

The subjects of investigations were diamond catalysts produced by various methods of modification of the initial diamond nanopowders synthesized by the ALIT Company using the detonation of oxygen-deficient explosives.

Thermodesorption mass-spectra of water, atomic and molecular hydrogen were taken on a MI 1201 mass-spectrometer in the temperature range from 20 to 600 °C [2].

Electrochemical studies of the oxygen reduction and hydrogen oxidation were conducted using the P-5848 potentiostat in a 0.5 M solution of sulphuric acid in an oxygen- or hydrogen-saturated atmosphere [1, 3, 5].

The experiments were performed on electrodes of three types:

- film electrodes applied to a substrate of isotropic graphite;
- gas-diffusion floating electrodes with a thin layer of promoted;
- rotating disk electrode of isotropic pyrographite having a thin layer of palladium precipitation (quantity of 0.001%) diamond nanopowders.

The parameters of the electrical oxidation of hydrogen and reduction of oxygen were compared using the materials like AD-100 hydrophobic carbon-black, ASM 1/05 grade statically synthesized diamond submicron powders, tungsten and vanadium carbides.

The measure of electrocatalytic activity of the powders was the exchange current density (i_{ex}), which was found by extrapolation of hydrogen over-current density curves to zero. superpotential.

The development of diamond catalysts involved special two-stage treatment of the diamond nanopowder surface, the so-called modifications. Figure 1 gives the schematic of the reception of electrode materials. As is seen from the schematic, the hydrogen electrode was made from special heat-treated treatment in the hydrogen environment [6].

The oxygen electrode was made from precipitation by a microquantity of the palladium also contributes to the diamond surface.

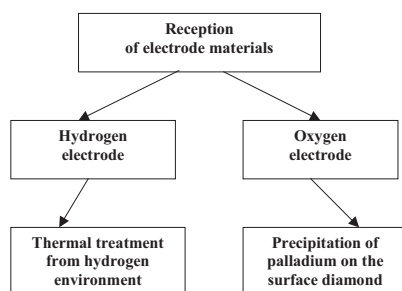


Figure 1. The schematic of the reception of electrode materials.

2.1. Results and Discussion

It has studied process of hydrogen electrooxidation with initial surface diamond (1) and after heat-treated (2) from concentration of sulfuric acid (Fig. 2).

It follows that the special heat-treated treatment in hydrogen environment has allowed us increased exchange current density by a factor of 1,8–2,0. At concentration change from 0,1 to 1,0 N exchange current density grows. At concentration change from 1,0 to 4,0 N exchange current density remains practically constant. Therefore, concentration of sulfuric acid equal 1,0 is optimum.

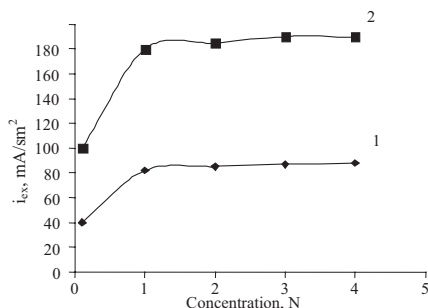


Figure 2. The exchange current density of hydrogen electrooxidation from of diamond (1) and after heat-treated (2) from concentration of sulfuric acid.

Figure 3 compares the exchange current densities on the initial nanodispersed diamond (4), modified nanodispersed diamond (after heat – treated treatment)(5), acetylene black AD-100 (1) and on the known catalysts tungsten (2) and vanadium (3) carbides. The specific surfaces of all samples of the powders were about 140 m²/g. The exchange current density on modified diamond nanopowders is higher than that on tungsten or vanadium carbides by a factor of 1.6.

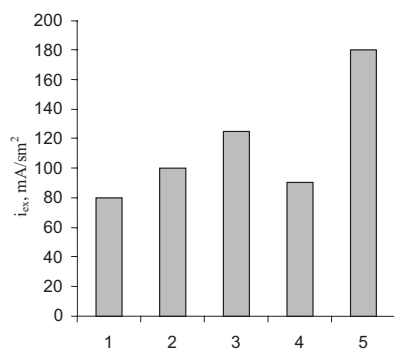


Figure 3. The exchange current density of hydrogen electrooxidation from acetylene black AD-100 (1), WC(2), VC(3), the initial nanodispersed diamond (4), the initial nanodispersed diamond after heat – treated treatment (5).

This two-stage heat-treated treatment has allowed us to produce an active layer on the diamond surface that catalyzes the hydrogen oxidation, to give effective catalysts for hydrogen electrodes.

Electrochemical oxygen reduction was studied on initial and precipitation diamond surface with a microquantity (0.001%) of palladium.

The cathode potentiodynamic curves of electroreduction of oxygen from the surface of the initial nanodispersed diamond (1) and initial nanodispersed diamond after precipitation of palladium (2) were presented. (Fig. 4). It is shown, that electrode catalytic activity precipitation palladium electrode increased into 1,5–2,0. Specific activity with romoted palladium nanodispersed diamond is equal to value 1.0 A/g to active weight.

One of informative methods of an directions of the mechanism of oxygen electroreduction is the method of a disk rotating electrode with a ring.

Figure 5 shows the cathode potentiodynamic curves of electroreduction of oxygen from the surface of nanodispersed diamond with palladium for different electrodes rate: $n = 640$ t./min., 2–2000 t/min, 3–3000 t/min.

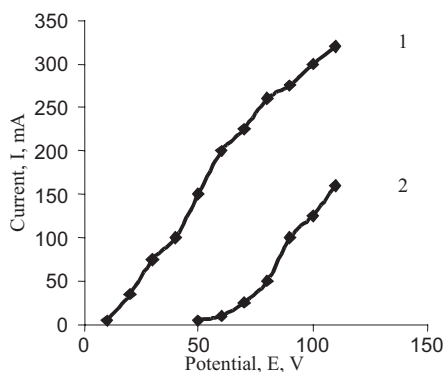


Figure 4. The cathode potentiodynamic curves of electroreduction of oxygen from the surface of the initial nanodispersed diamond(1) and initial nanodispersed diamond fter precipitation of palladium(2).

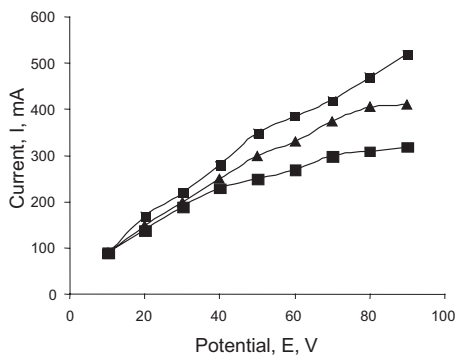


Figure 5. The cathode potentiodynamic curves of electroreduction of oxygen from the surface of nanodispersed diamond with palladium for different electrodes rate: $n = 640$ t./min., 2– 2000 t/min, 3–3000 t/min.

Tafel constant is equal to $dE/d\lg I$ more that 1,5 order make inclination of current change at potential interval 0,5–0,3V 120–130 mV, close to $2RT/f$.

The received value inclinations closes Tafel inclinations (60 and 120 mV), which characteristic for reaction of the first order to oxygen for smooth electrodes.

Figure 6 compares the current exchange densities on the AD-100 hydrophobic carbon- black (1), the initial diamond nanopowders (2), diamond powders of 0,7 μm (3), nanopowders with palladium precipitation (4). It is seen that the exchange current density after the promotion with palladium to be increased by a factor of 3 and 1.3 as compared with the initial diamond nanopowders and AD-100 carbon-black.

The kinetic of catalytic oxygen reduction is closely connected with chemical condition of surface nanodispersed diamond.

The physico-chemical properties of surface initial diamond. are, in their turn, due to chemical composition of the powder surface, the nature of adsorption processes proceeding on the surface of their [7, 8].

It is shows the thermodesorption spectra of water, atomic and molecular oxygen mono-two-oxide from the surface of initial diamonds taken in 20–600⁰. Figure 7 shows the thermodesorption spectra of water from the surface the initial diamond (1) and diamond after palladium precipitation (2). It is seen from the figures that there is a great difference in quantity of water on the initial and modified surfaces of diamonds. The water quantity, which desorbed with precipitation palladium diamond increased in 5.

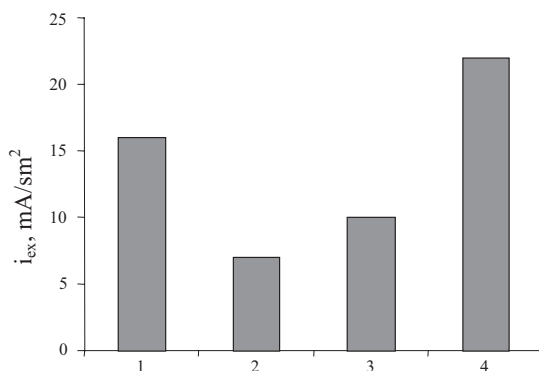


Figure 6. The exchange current density of oxygen electroreduction from acetylene black AD-100(1), initial nanodispersed diamond(2), diamond ASM 1/0,5(3), initial nanodispersed diamond after palladium precipitation (4).

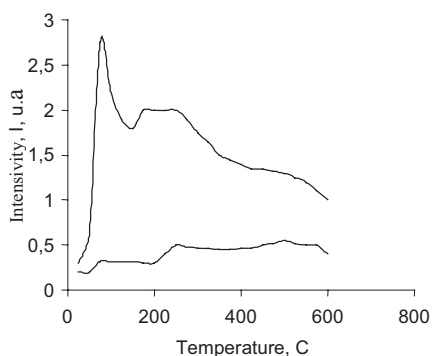


Figure 7. Thermodesorption spectra of water from the surface: the initial nanodispersed diamond (1), the diamond after promoted palladium(2).

Figure 8 shows the thermodesorption spectra of atomic oxygen from the surface the initial diamond (1) and promoted palladium diamond (2).

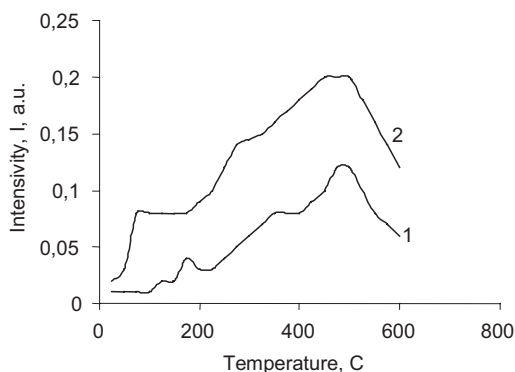


Figure 8. Thermodesorption spectra of atomic oxygen from the surface: the initial nanodispersed diamond (1), the initial nanodispersed diamond after precipitation of palladium (2).

The amount of adsorbed atomic oxygen also changes considerably. Maximum quantity of atomic oxygen was observed temperature 500°C. It is established that as atomic oxygen is connected to a diamond surface. The atomic oxygen are formed at dissociations of chemical connected OH⁻ groups.

Thus, palladium-promoted diamond nanopowders are effective catalysts for oxygen electrodes.

3. Conclusions

1. This special heat-treated treatment in hydrogen environment has allowed us to produce an active layer on the diamond surface that catalyzes the hydrogen oxidation.

2. The exchange current density on modified diamond nanopowders is higher than that on tungsten or vanadium carbides by a factor of 1.6.

3. The promotion by a microquantity of the palladium to the diamond surface allowed more than 1.5 order to increase electrodes activity. Specific activity promoted palladium nanodispersed diamond is equal to value 1.0 A/g to active weight.

4. Precipitation palladium diamond nanopowders has been high quantity of atomic oxygen. The atomic oxygen are formed at dissociations of chemical connected OH⁻ groups.

5. Precipitation palladium diamond nanopowders are effective catalysts for oxygen electrodes.

6. The special heat-treated treatment in hydrogen environment has allowed us effective catalysts for hydrogen electrodes.

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TECHNICAL AND TECHNOLOGICAL METHODS OF REALIZATION OF STEAM CATALYTIC CONVERSION OF NATURAL GAS WITH A METHANE-WATER PROPORTION CLOSE TO STOICHIOMETRIC RATIO

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Abstract. The experimental results and also results of industrial tests on realization of the catalytic conversion of the natural gas in a warmed pipe with the purpose of reception of a gas mix of CO and H₂ without H₂O and CO₂ are presented. This mix are called as technological gas or synthesis-gas or regenerative gas - depending of using method. The reaction $\text{CH}_4 + \text{H}_2\text{O} = 3 \text{H}_2 + \text{C}$ (1) was carried out in stoichiometric ratio or with the ratio close to stoichiometric ($\text{H}_2\text{O}/\text{CH}_4 < 1.5$). Technologies and outline descriptions of designs of corresponding devices are presented.

Keywords: methane, natural gas, hydrogen, oxide carbon, the nickel catalyst, inhibitor, a warmed pipe.

1. Introduction

Reception of a gas mix of CO and H₂ from hydrocarbon raw material is a base process of chemical, oil-and-gas and metallurgical industry. In depending on use the mix of CO and H₂ are called technological gas, synthesis-gas, regenerative gas. The basic raw material to produce the mentioned mix are natural gas and associated petroleum gas. Hydrocarbons of these gases are oxidized with H₂O or (and) CO₂ accordingly forming the mix of CO and H₂. The most part of natural gas and associated gas contains paraffin hydrocarbons and their reactions with water look as follows:

- (1) – $\text{CH}_4 + \text{H}_2\text{O} + n \text{H}_2\text{O} = 3 \text{H}_2 + \text{CO} + n \text{H}_2\text{O} + 206,4 \text{ kJ/mol}$
- (2) – $\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} + n \text{H}_2\text{O} = 5 \text{H}_2 + 2 \text{CO} + n \text{H}_2\text{O} + 347, \text{ kJ/mol}$
- (3) – $\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} + n \text{H}_2\text{O} = 6 \text{H}_2 + 3 \text{CO} + n \text{H}_2\text{O} + 406,1 \text{ kJ/mol}$
- (4) – $\text{CH}_4 + \text{CO}_2 + n \text{H}_2\text{O} = 2 \text{H}_2 + 2 \text{CO} + n \text{H}_2\text{O} + 248,3 \text{ kJ/mol}$

We can see, that reactions go with absorption of heat and their endothermic effect is high enough. There is a reaction of incomplete combustion of methane: $\text{CH}_4 + \text{O}_2 = 2\text{CO} + 2\text{H}_2$ (5). Full exergic analysis of technological schemes where technological gas is used, the scheme with reaction (1) gives greater exergic coefficient of efficiency [1,2] in comparison with the scheme using reaction (5).

Reactions (1) - (4) pass on the catalyst in a warmed pipe in a recuperative mode. The main disadvantage of considered process is the necessity to use the surplus of H₂O [1]. The surplus is defined with molar ratio: $(\text{mol H}_2\text{O})/\text{C} = N$. Depending on operation conditions, tubular furnaces designs and the used catalyst $2 < N < 7$. Clear that use of H₂O surplus greatly increases power consumption of hydrocarbons conversion process as a whole. Necessity of increase N is connected with allocation of carbon on the catalyst (the mechanism of carbon allocation is

described in [3,7,8,9]). Reactions (1) - (4) are total – consisting of some chemical transformations, but this number can be divided on two groups. Border between two groups of transformations, this formation of free carbon [7,8,9]. The first group of chemical transformations will be united endothermic by reaction: (6) $C_aH_b = aC + b/2 H_2 + \Delta H$ ($\Delta H=75\text{kJ/mol}$ for $a=1$ and $b=4$). The second group of transformations is united by reaction (7): $C + N H_2O = C+H_2 + (N-1) H_2O + \Delta H$ (endothermic effect $\Delta H=131\text{kJ/mol}$). Real realization of reactions (1) - (4) demands identical speed of formation of carbon on reaction (6) and speeds of gasification of carbon on reaction (7). If speed of reaction (6) exceeds speed of reaction (7) carbon starts to be allocated and destroys the catalyst. According to statistical sense of thermodynamics for carrying out of reactions (2) - (5) in stoichiometric relationships it is necessary high temperature or significant surplus H_2O are required. Distribution of temperature of a wall and reacting gas in a warmed pipe filled completely is shown by the catalyst on Fig. 1 [3]:

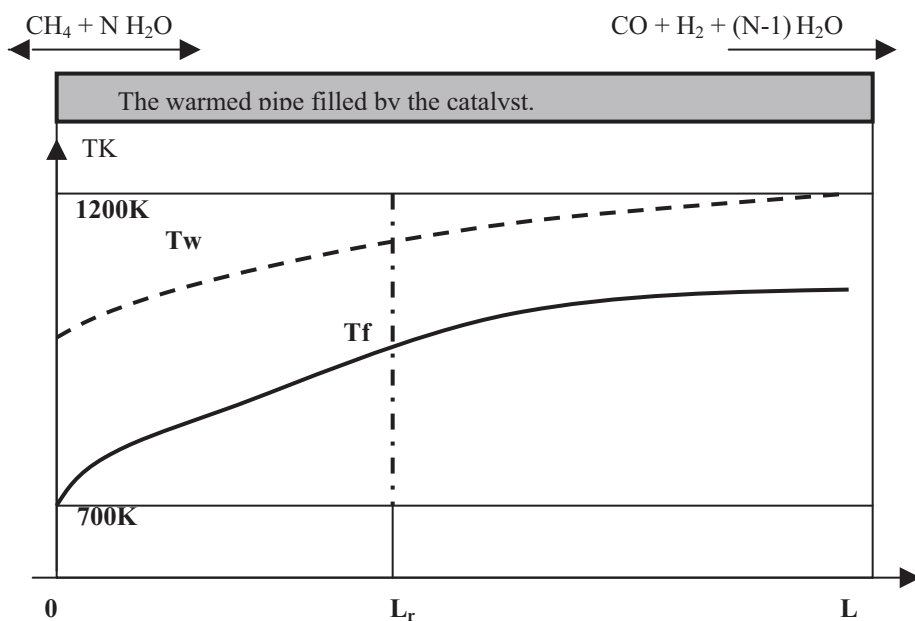


Figure 1. Distribution of temperature of a wall and reacting gas in a separate pipe of the furnace of conversion natural raza: T_w – temperature of a wall, T_f – temperature of gas.

In Fig. 1 in a pipe on a site $0L_r$ reacts more than 50 % of hydrocarbons participating in chemical transformations, therefore temperature up to enough high level to lift it is impossible. Therefore instead of formal calorific effect ΔH , heat representing quantity absorbed in stoichiometric ratio to system, we shall present effective thermal effect Q , as quantity of heat absorbed during chemical reaction carried to weight of all products of reaction formed after achievement of an equilibrium condition. Effective thermal effect Q we shall present in the form of function $Q = f(n)$ where $n = (N-1)$ and dimension kJ/mol we shall replace on kJ/kg change of effective thermal effect Q depending on n for reactions (1) - (4) will look as follows:

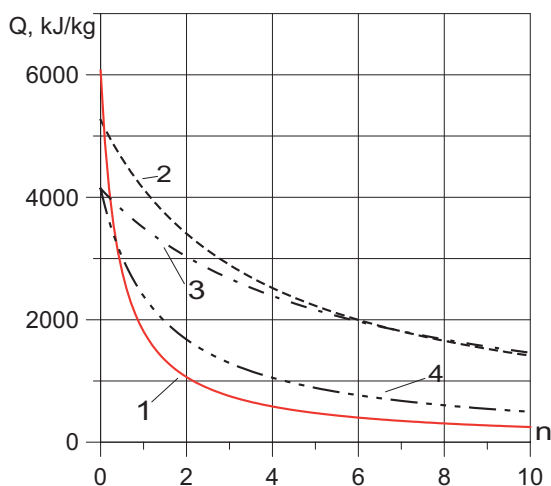


Figure 2. Dependence of effective thermal effect Q on surplus of an oxidizer n .

The effective thermal effect decreases with increase n and it allows a thermal stream to provide on an internal surface of a pipe passage of reaction (7). It will be coordinated with statistical sense of thermodynamics – speed of reaction increases with increase in quantity of one of components in unit of volume.

2. Experimental

In IVT AN (1977-80) there was a task in view of reception of pure regenerative gas, for desulphurization an ionized additive on MHD electric power station working on a coal. For reception of pure regenerative gas reactions (1) and (4) have been chosen. As the initial mix of gases on a number of the physical and chemical reasons cannot be heated up to temperature 1200K up to a reactionary pipe the experimental reactionary pipe all over again was filled inhibitor and only then with the nickel catalyst. On Fig. 3 the device of an experimental pipe catalytic is shown to conversion of methane and characteristic distributions of temperatures and concentration:

The experimental assembly which is described in [3] has been made. The basic experimental object – a tubular reactor of conversion of methane represented a warmed pipe in length of 1,5 m and with internal diameter 56 mm. On an input, the reactor was filled inhibitor with a nozzle from spheres ZrO_2 in diameter 19mm. The length of a layer inhibitor 0,46 m. Other part of a pipe was filled with the nickel catalyst. The nickel catalyst is Rashig rings in the size: $15 \times 11 \times 6$ mm. Were measured: temperature of a wall of a pipe, temperature of reacting gas on length of a pipe and on radius of a pipe, concentration of reacting and formed gases. Mass charges of reacting products: $GCH_4 = 0.1 - 0.3$ g/s, $GH_2O = 0.1 - 0.5$ g/s, $GCO_2 = 0.15 - 0.5$ g/s. The capacity of heating brought to a reactor 2000 – 5000 Wt. On Fig. 3 some results of experiments are represented. In figure it is visible, that the most part of chemical transformations occurs on a site after border between the catalyst and inhibitor. This site is named: zone of the most active reaction (ZMAR). Physical sense of this zone – the greatest quantity of heat should be brought in the fixed zone of the most active reaction.

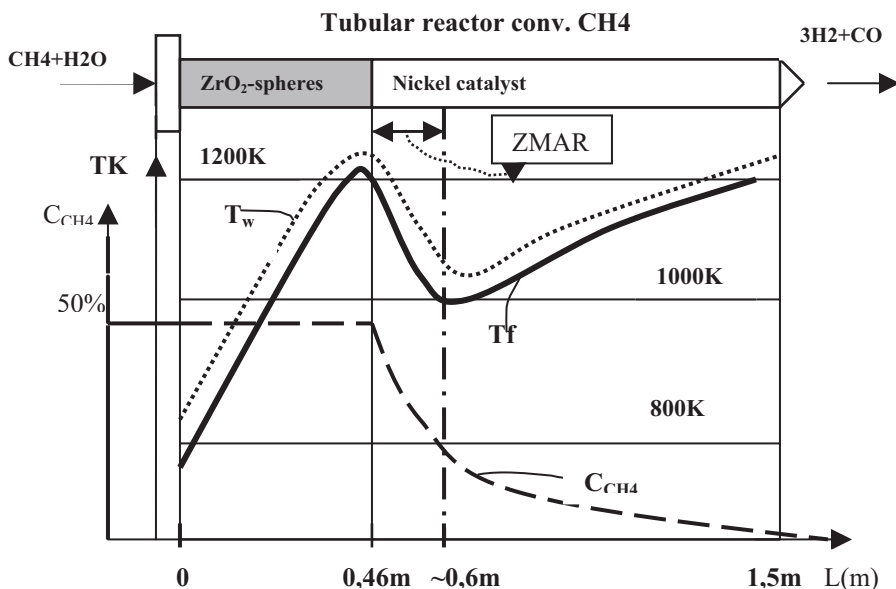


Figure 3. distribution of temperature of a wall (T_w), temperatures of reacting gas (T_f) and concentration of methane (C_{CH_4}) on length of an experimental warmed pipe.

The technical decision of this condition in an industrial pipe of conversion of natural gas will allow to lead conversion in stoichiometric ratio the attitude or close to them ($N < 1,5$ or $n < 0,5$). The first decision assumed creation on one pipe of the industrial sizes (length nearby 10) loading inhibitor and the catalyst to similarly experimental reactor. On this pipe to establish heating so that the temperature of a wall on all length was a constant ($T_w = \text{const.}$) [4]. Clearly, that at such heating in ZMAR the greatest possible quantity of heat will be brought. However this way demands the individual heating device.

To use phenomenon ZMAR in industrial warmed pipes of tubular furnaces of conversion of natural gas (TFCNG) the device of alternation inhibitory and catalytic layers in a separate pipe [5,6] is offered. On Fig. 4 the doodling - conditional image of an industrial pipe in length $L > 10\text{m}$ is represented. Physical sense of process which is illustrated on Fig. 4 following: the mix of reacting gases acts in a pipe and without chemical transformations heats up on inhibitor to the set temperature to close temperature of a wall. There is a layer of the catalyst where the temperature decreases on the set size 100K further. After the catalyst the nozzle is again established inhibit, and the mix of gases without reaction heats up. And so until hydrocarbons will react fully and all. On Fig. 4 it is presented so: I a layer inhibitor, further II layer of the catalyst, further III layer inhibitor, further IV layer of the catalyst, further V a layer inhibitor, VI layer of the catalyst, VII layer inhibitor, VIII layer of the catalyst – hydrocarbons have reacted process of formation CO and H_2 is finished. The broken line on Fig. 4 designates change of temperature T_f on length of a pipe.

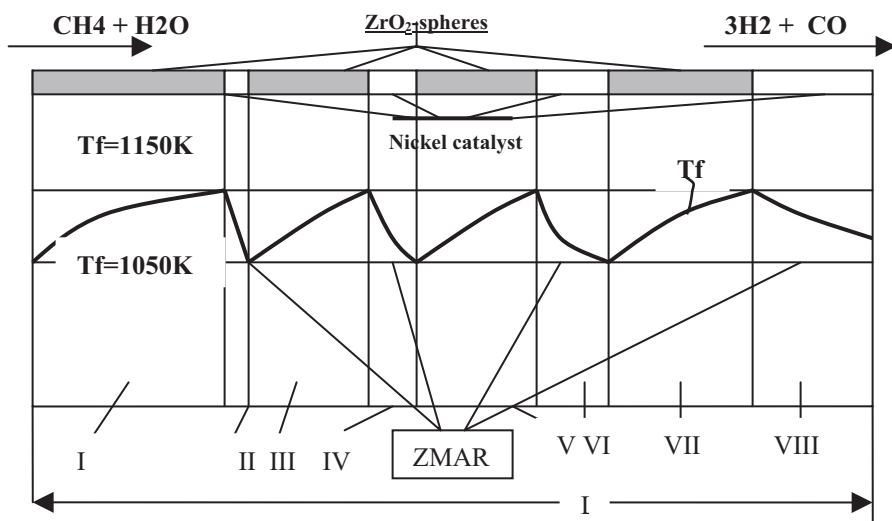


Figure 4. Device of alternation inhibitory and catalytic nozzles in a separate pipe of the tubular furnace of conversion of natural gas.

Such algorithm of an arrangement inert and catalyst was used for loading separate pipes industrial TFCNG at the Novocherkassk factory of synthetic products (H3CII) and Oskolsky electrometallurgical combine (OЭМК). It was projected TFCNG in Ukraine for a blast furnace instead of blasting by natural gas. Mass charges on these TFCNG were $GCH_4=250 - 350$ g/s. Tests have passed successfully per 1989-1990.

Calculation of lengths of layers at the task of regime parameters was spent on the basis of the standard techniques of definition heat transmission in disperse layers of nozzles with drains of heat and without drains of heat, and were based on the given experiments. It is necessary to emphasize, that success of tests depends on correctness of calculation of lengths of layers of nozzles.

For calculation of length inhibitory nozzles expression was used:

$$L_{ING} = d_{ef} Pe_r \frac{Bi + 4}{8Bi} \ln \frac{(Bi + 4)^2}{2(Bi^2 + 4Bi + 8)} \frac{T_w - T_0}{\Delta T} \quad (1)$$

Here d_{ef} – effective diameter of a granule; Pe_r – effective radial number Pickle; Bi – criterion Bio; T_0 – temperature of a gas mix on an input in a layer; T_w – temperature of a wall; ΔT – the set increase or reduction of temperature of a reacting gas mix from an input up to an output from a layer.

For calculation catalytic nozzles it was used quasihomogeneous model. For conditions of a separate pipe it is possible to write down following system of the equations:

$$\left\{ \begin{aligned} w \sum_i c_i c_{pi} \frac{\partial T}{\partial x} &= \lambda_a \frac{\partial^2 T}{\partial x^2} + \lambda_r \left(\frac{\partial^2 T}{\partial x^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) - \Delta H \omega(T); \\ \frac{\partial}{\partial x} (w c_i) &= v_i \omega(T); \\ i &= CH_4, H_2(CO_2), H_2, CO; \\ \frac{\partial}{\partial x} (w \sum_i c_i) &= 2 \omega(T). \end{aligned} \right. \quad (2)$$

In (2) following designations are accepted: T – temperature of a gas mix; x and r – longitudinal and radial coordinates; w – linear speed of a gas mix; c_i and c_{pi} – molar concentration and a thermal capacity of i -th component of a gas mix; λ_a and λ_r – longitudinal and radial effective factors of heat conductivity; ΔH – formal thermal effect of reaction (1); $\omega(T)$ – volumetric speed of reaction (1); v_i – stoichiometric factor of i -th component.

The Important component of calculation have λ_a and λ_r in which processes of carry of heat in a disperse layer are considered all.

In the given technique speed of reaction was defined on the equation:

$$\omega(T) = k_0 C_{CH_4} \exp(-E/R_g T),$$

where k_0 – preexponential multiplier; C_{CH_4} – current concentration of methane; E – energy of activation; R_g – a universal gas constant. Sizes k_0 and E were defined by practical consideration in the allocated experiments.

Boundary conditions for system of the equations (2) are:

$$\left\{ \begin{aligned} T &= T_0; \quad c_i = c_{i0}; \quad x=0; \\ -\lambda_r \frac{\partial T}{\partial r} &= k(T_{pb} - T), \quad r=R. \end{aligned} \right. \quad (3)$$

Here k – factor of a heat transfer « products of combustion of external heating of a pipe – a wall of a pipe – a layer of the catalyst or inhibitor»; R = radius of a pipe; T_{pb} – temperature of products of combustion of external heating of a pipe (the temperature is supposed a constant).

The note: In above presented text it was not considered thermodynamic equilibrium concentration and collateral reactions, a number of known assumptions which at concrete application of the present techniques, should be considered is made.

3. Conclusions

During laboratory experiments and industrial tests a number of effects improving as a whole process of conversion is established. For example, it concerns forms of granules of a nozzle. A spherical nozzle in some cases more technologically traditionally used forms. The catalyst made of Rashig rings, harmfully affects in conditions ZMAR since stagnant zones are created. The effective utilization of some the phenomena demands additional experimental researches.

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MAGNETIC & THERMODYNAMIC STUDIES OF CoO (I) & CoO (II)

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Abstract. Two forms of CoO have been prepared from spec. pure Co metal and CoCO₃ and the magnetic susceptibility of CoO(I) and CoO(II) examined over a temperature range 300–700 deg. K. The magnetic data of CoO(II) have shown an anomalous temperature dependence of that in this temperature range CoO(II) passes into CoO(I). This result is in conformity with Mossbauer spectra. Furthermore, D.T.A and temperature dependence of magnetic susceptibility of CoO(II) arises from a first order phase transition.

The magnetic data of CoO(I) and CoO(II) have been correlated with a two sublattice model and exchange parameters evaluated.

Keywords: D.T.A.-Differential Thermal analysis; magnetic susceptibility, Mossbauer spectra; sub-lattice

1. Introduction

Cobaltous Oxide is known to be a good catalyst for oxidation reactions. In recent times, existence of two forms of cobaltous oxide possessing different physico-chemical properties have been reported¹. The form I, CoO(I) (prepared by heating cobalt metal in carbon dioxide at 1000°C) has a NaCl structure and the form II, CoO (II) (prepared by decomposing cobalt carbonate at 300°C in vacuum) has a NaCl structure with half of its (+)ve ion sites and half of its (-)ve ion sites vacant. The density measurements¹ have shown that CoO (I) has a density of 6.4 gms / cm³ whereas CoO (II) has a density of 4.8 ± 0.5 gms per cm³. The same authors¹ have also found that CoO (II) transforms noticeably to CoO (I) at about 300°C, giving CoO (I,II) – a mixture of form I and II.

It remains to be investigated which of the two forms of cobaltous oxide is mainly responsible for the catalytic activity, through a study of the physical properties of the two forms and their catalytic activities.

In the present paper the results of magnetic measurements and Differential Thermal Analysis (DTA) are presented.

2. Experimental

CoO (II), CoO (I), CoO (I,II) have been prepared following the methods described by Ok and Mullen¹. In addition to this, CoO(I) and CoO(I,II) have also been prepared by a second method.

The magnetic susceptibilities of CoO(II), CoO(I), CoO(I,II) have been measured² over the temperature region 300⁰ – 700⁰K. The DTA measurements on CoO (II) in the temperature region 300⁰ – 850⁰K in vacuum and Ar. Atmosphere were done in sealed Pyrex glass ampule by using the conventional DTA apparatus.

3. Results

The results of magnetic susceptibility measurement and DTA are shown in figure 1 & 2 respectively.

The magnetic susceptibility data of the two forms of CoO and the mixture show that CoO(II) has got the highest magnetic susceptibility value at room temperature (5231×10^6 gms/mole), in comparison to the room temperature susceptibility values of CoO(I) (4684×10^6 gms per mole) and CoO(I,II) (4762×10^6 gms/mole). This arises from the low density of CoO(II) compared to CoO(I) and CoO(I,II).

Along with the temperature dependence of magnetic susceptibility of CoO(I,II), CoO(I) and CoO(II), the magnetic susceptibility data of LaBlanchetais³ has also been shown in Figure 1. The sample-to-sample variation in the region $300^\circ - 600^\circ$ K indicates that the magnetic susceptibility depends profoundly on the sample preparation. The plot of X_m vs T in CoO(I,II) follows a linear relationship whereas CoO(I) shows a slight curvature increases in the case of CoO(II). Further, in CoO(II) the susceptibility shows an anomalous behaviour in the temperature region $550^\circ - 600^\circ$ K indicating that in this temperature range CoO(II) slowly passes into CoO(I). Beyond the transition region all the samples show a similar behaviors. This result is in conformity with the Mossbauer data¹. The transition observed in CoO(II) is not of magnetic origin since the sample is paramagnetic both below and above the transition temperature. But, the large density difference between the two forms suggests that the transition is probably of first order. The evaluation of exchange parameter appears difficult due to the magnetic anomaly in the region $300^\circ - 800^\circ$ K.

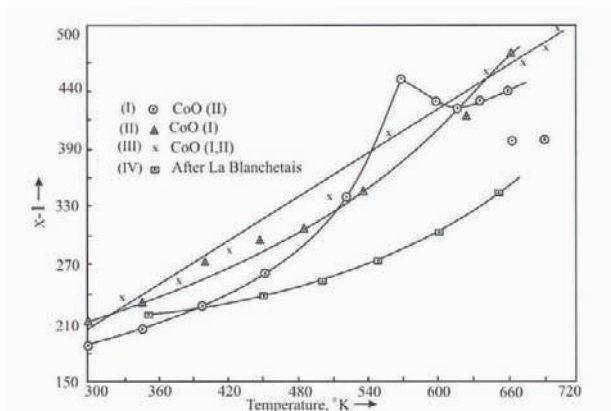


Figure 1. The temperature dependence of susceptibility of cobalt oxide.

The DTA measurements on CoO(II) shows that the endothermic pattern of thermograph changes at about $550 \pm 5^\circ$ K indicating a change in the form of CoO. such a change might be due to contraction of the lattice.

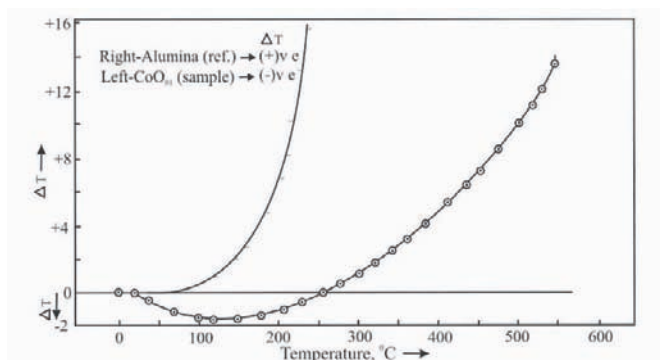


Figure 2. DTA thermograph of CoO (II).

On the basis of the observed differences in the physical properties of the two specimen of CoO, the catalytic activity is being investigated by us.

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STRUCTURE AND FORMATION OF FILMS OF ZIRCONIA-BASED SOLID ELECTROLYTE

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Abstract. Films of zirconia-based solid electrolytes were prepared by the ion-plasma sputtering method. Scanning and transmission electron microscopy methods were used to analyze their structure and processes of their formation. It was found that films of $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ and $\text{ZrO}_2 - \text{Sc}_2\text{O}_3$ systems had a nanocrystalline structure. The zirconia-based films were characterized by a columnar structure. A model describing the formation of pores and submicropores during the growth of films of $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ and $\text{ZrO}_2 - \text{Sc}_2\text{O}_3$ systems was proposed and discussed.

Keywords: structure of films, films of zirconia-based solid electrolytes, ion plasma sputtering, scanning electron microscope, transmission electron microscopy.

1. Introduction

It is known that an important advantage of the ion-plasma sputtering method is the possibility to produce films of multicomponent materials, whose chemical composition coincides with the one of the target [1]. Bearing this in mind, films of solid electrolytes based on zirconium dioxide, which was stabilized to its cubic modification by Y_2O_3 and Sc_2O_3 additions were prepared using the ion-plasma sputtering method.

The structure and the formation of films of a zirconia-based solid electrolyte, which were prepared by ion plasma sputtering, were studied using scanning and transmission electron microscopy methods.

2. Experimental and Discussion

The structure of films of zirconia-based solid electrolytes was analyzed in a scanning electron microscope. It was found that both one- and multilayer films (Fig. 1a, 1b) of zirconia, which was stabilized to its cubic modification, up to 10 μm thick had a columnar structure, that is, consisted of mutually adjoining crystallites, which generally were oriented perpendicularly to the film surface. The observed deviation of the crystallites from the normal direction to the film plane was not over 15° and was explained by the mutual misorientation of the target and the substrate.

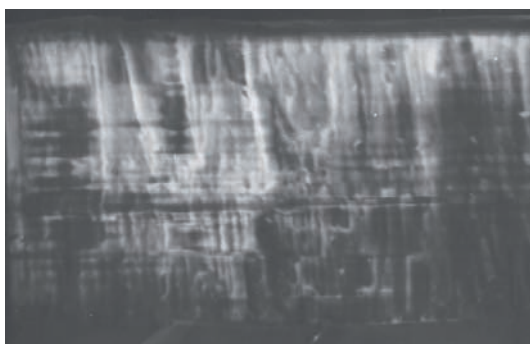


Figure 1a. x5000



Figure 1b. x 5000

Figure 1a. Electron microscopic image of a fracture of a multilayer film of a zirconia-based solid electrolyte.

Figure 1b. Electron microscopic image of a fracture of a monolayer film of a zirconia-based solid electrolyte.

A significant property of the multilayer films, namely the structural “independence” of adjacent layers, was revealed. This property showed up as an offset of structural elements and grain boundaries between layers. Therefore, it was possible to control structure-sensitive parameters of the solid-electrolyte films.

Considering the obtained experimental data, it is possible to propose a model of the formation of a porous structure of the films of zirconia-based solid electrolytes. The model assumes the formation of pores and submicropores when vacancies, which are trapped during sputtering of the solid-electrolyte films (the sputtering temperature was $T_f < 0.3T_{\text{melt}}$), pass to sinks and then condense [2,3,4,5]. The sinks are boundaries between the crystallites forming the film structure.

The transmission electron microscopy was used to study the initial stage of the formation of the films of zirconia-based solid electrolytes, which were prepared by ion plasma sputtering on a glass-ceramic substrate having a thin (~ 10 nm) layer of amorphous carbon.

It was found that at the initial stage of its formation the film of the zirconia-based solid electrolyte consisted of nanocrystallites arranged randomly or in some order. The nanocrystallites had an irregular round shape and were ~ 40 nm in size on the average. Ordered nanocrystallites generally formed squares, but sometimes they were shaped as parallelograms (Fig. 2). The nanocrystallites had a kind of self-organization.

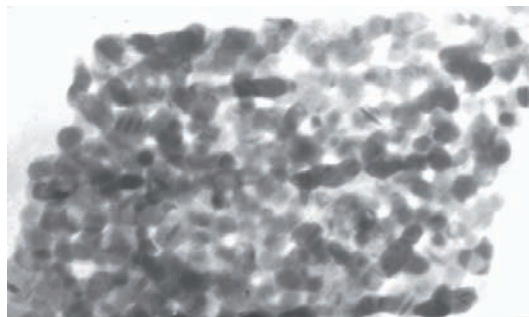


Fig. 2a x 200000

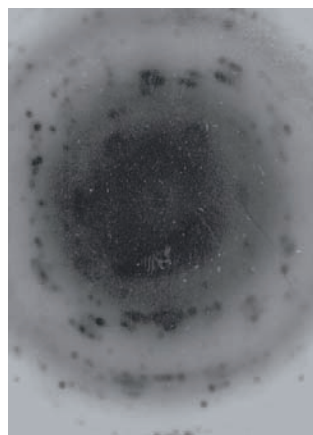


Fig. 2b

Figure 2a. Ordered nanocrystalline structure of a film of a zirconia-based solid electrolyte in the form of a parallelogram.

Figure 2b. Electron diffraction pattern of an ordered nanocrystalline entity.

An electron diffraction study of the ordered nanocrystalline entities demonstrated that the electron patterns were similar to those of block crystals. As distinct from the block crystals, the ordered nanocrystalline entities had discontinuities (Fig. 2a). The electron patterns of the ordered nanocrystalline entities suggested a high orientation coordination of their constituent nanocrystallites (Fig. 2b).

Since the nanocrystallites were separated from the substrate with a layer of amorphous carbon, one might think that the ordered arrangement of the nanocrystallites was due to an auto-orientation mechanism, which operated at all stages of the growth of the ordered nanocrystalline forms of the films of the zirconia-based solid electrolyte.

3. Conclusions

The simultaneous analysis of the results of the study into the structure and the formation of the solid-electrolyte films led to the following conclusion: the nanocrystalline structure of the solid-electrolyte films at the initial stage of their formation caused the appearance of a columnar structure of the films of the zirconia-based solid electrolyte during their sputtering.

An ordered arrangement of the nanocrystallites was due to an auto-orientation mechanism operating at all stages of the formation of a nanocrystalline ordered structure of the films of solid electrolytes in $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ and $\text{ZrO}_2 - \text{Sc}_2\text{O}_3$ systems.

The use of multilayered films of zirconia-based solid electrolytes in fuel cells is more promising than the use of one-layer films.

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EPR SPIN PROBE STUDY OF CARBON NANOPARTICLES HYDRATION PROPERTIES IN AQUEOUS DISPERSIONS

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Abstract. The relationship of hydration properties of carbon nanoparticles in aqueous dispersions and stability of these dispersions with respect to aggregation have been studied using EPR spin probing of frozen dispersions. Aqueous dispersions of shungite carbon nanoparticles at different concentrations and aqueous colloids of fullerenes C_{60}/C_{70} have been compared. Characteristic features of the bounded water have been shown to correlate with a decrease of aqueous dispersions stability to aggregation.

Keywords: Shungite, Carbon nanoparticles, EPR, aggregation

1. Introduction

One of the promising trends in developing carbon nanomaterials is aimed at their biomedical applications that imply interaction with water. Besides, employing water as a disperse medium in present-day technologies of carbon material engineering is preferable from the ecological point of view despite the apparent hydrophobicity of carbon. The ultrasonic procedures of preparation of carbon nanoparticles (fullerene) water dispersions even with no use of surfactants [1] bring up the question of the dispersions stability to aggregation. Namely, dilute C_{60} fullerene solution (< 0.1 mg/ml by weight) is a brownish transparent colloid solution that contains both isolated hydrated fullerenes, and their hydrated fractal clusters of different size. The least clusters are of 6–8 nm diameter containing 13 hydrated C_{60} molecules while the largest are up to 60 nm [2]. Increase of C_{60} concentration decreases stability of the colloid solution to aggregation. Coagulation of fullerenes by inorganic electrolytes is shown to occur according to the Schultze-Hardy rule, but solution stability is described within the framework of DLVO theory of hydrophobic colloids [3]. Fullerene hydration and stability is a rather complex issue. The most widely accepted and supported hydration model is the model of donor-acceptor water-fullerene complexes involving several solvent layers [2]. Formation of specific hydration shells around nanoparticles that prevent their rapid coagulation is likely to be an important factor of their stability. Thus, the properties of those hydration shells are of primary significance in the understanding the mechanism of stability.

In recent years shungites have been attracting much attention due to the prospect of their various industrial and biomedical applications [4]. Special attention to shungites is connected with the reported [5] presence of fullerenes and nanostructures in them. Also, the possibility to disperse shungites into aqueous medium in the same way as in the synthesis of fullerene dispersion should be mentioned [1,6].

Wide variety of experimental techniques and data remain insufficient to explain characteristics even of pure water. The fraction of water modified by the particles surface in dispersions is very small and its properties differ only slightly from that of bulk water. This brings about additional complexity to the study of the properties of nanocarbon hydration layers.

Using ESR spin probe technique one can allow for the contribution of bulk water due to its preferential freezing as compared to the fraction of water modified by the dispersed particles surface [7,8]. Surface water molecules and spin probe localized in that water retains its mobility at lower temperatures than bulk water molecules do and EPR signal from these spin probes dominates in spectrum. Specifically the sequence of freezing of water attached to different chemical groups at the surface is as follows: water at nonpolar, polar and, finally, at charges surface sites [9,10].

This study is aimed at elucidation of the role of water bounded at shungite carbon nanoparticles (ShC) in their dispersions stability with respect to aggregation at different ShC concentrations. The properties of bounded water were compared to those of water modified by C_{60}/C_{70} fullerene dispersion.

2. Materials and methods

Aqueous dispersions were prepared from shungite type I (Shunga deposit) and fullerene powder produced by "Intellect Co". St.-Petersburg, using the procedure developed elsewhere for fullerenes [1]. The latter contains $C_{60}/C_{70} = 83/16$ and about 1wt.% of higher fullerenes.

Hydrophilic spin probe 4-Oxo- TEMPO (Sigma) of 0.1 mM concentration was introduced in water dispersions of ShC nanoparticles of different concentrations (0.1, 1.0 and 10 mg/ml). Paramagnetic spin probe like TEMPOL effectively dissolves in hydration water [7,8] owing to capability of polar and paramagnetic NO group of probe to form hydrogen bonds with water molecules.

Control experiments were performed for water solutions of C_{60}/C_{70} fullerenes (0.1 mg/ml), fullerene solution (0.1 mg/ml) containing 0.015 M NaCl, silica with 50 nm pores (1 mg/ml) and pure water. Spin probe EPR spectra were taken within 230-287 K temperature range with the step of 1-2 K on radiospectrometer EMX (BRUKER). Effective spin probe rotational correlation times τ_{cf} were determined from EPR spectra by the intensity ratio of low- and high-field spectrum components with an allowance for the variation of low-field line width [11]. Effective thermodynamic parameters (Gibbs energy ΔE , enthalpy ΔH and entropy ΔS) of the probe rotational activation were calculated for different dispersions and temperature intervals using Arrhenius coordinates. Variations of the spectrum isotropic superfine structure constant a_N , and parameter of the probe rotational anisotropy ε were also under study. a_N is sensitive to the nitroxide spin probe fragment interaction with water molecules, and ε is determined by the ratio of all three spectrum components [7,11] and characterizes orientational properties of surrounding solvent.

3. Results and Discussion

Figure 1 shows Arrhenius plots of the spin probe effective rotational frequency ($\log \tau^{-1}$ vs. $1/T$) in liquid and frozen colloid solutions and dispersions of carbon nanoparticles. The plots are presented for different concentrations of nanoparticles and for water. Linearization of individual segments of the plots ($T < 250$ K) allowed calculating the thermodynamic parameters of the spin probe motional activation. No significant difference in the spin probe motional activation parameters has been

observed within the temperature range of liquid state (taking into account the supercooling to -13°C in capillaries during freezing) ($\Delta E = 5,1 \pm 0,4$ kJ/mole, $\Delta H = 9,0 \pm 0,2$ kJ/mole, $\Delta S = 14 \pm 1$ J/mole·K) as the dynamics of the probe in the bulk solvent makes dominating contribution. The difference is just as insignificant within the temperature range of supercooling where experimental points were taken on raising the temperature of frozen solutions. The probe microenvironment viscosity increases noticeably at freezing of bulk water ($T < 260$ K). The signals of the probes localized in unfrozen water layer at nanoparticle surface remain in the probe spectrum as those probes are of the highest motility. Considerable differences in the rotational activation parameters are observed in every sample within 250-230 K temperature range (Table 1, Figure 1).

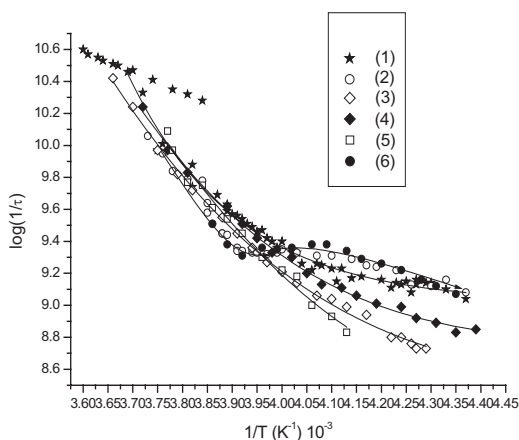


Figure 1. Arrhenius plots of the spin probe effective rotation frequency ($\log \tau^{-1}$ vs. $1/T$) for water and frozen colloid solutions and carbon nanoparticles dispersions of different concentrations: (1) – liquid water including supercooled water at -13°C and frozen water (experimental points within the temperature range of supercooling were taken on rising temperature); (2)– 0.1 mg/ml $\text{C}_{60}/\text{C}_{70}$; (3) – 0.1 mg/ml $\text{C}_{60}/\text{C}_{70} + 0.015$ M NaCl; (4) – 1 mg/ml ShC; (5) – 10 mg/ml ShC (unstable dispersion); (6) – 0.1 mg/ml ShC.

TABLE 1. Effective thermodynamic parameters of spin probe motional activation in frozen solutions ($T < 250$ K)

Solution content	ΔE , kJ/mole, (244K)	ΔH , kJ/mole	ΔS , kJ/mole·K
Water	6.9 ± 0.5	6.1 ± 0.2	-3.3 ± 0.3
Silica, 1 mg/ml	7.2 ± 0.5	6.6 ± 0.2	-2.5 ± 0.3
ShC, 0.1 mg/ml	6.7 ± 0.2	9.8 ± 0.1	12.5 ± 0.4
ShC, 1 mg/ml	7.3 ± 0.4	10.1 ± 0.3	11.6 ± 0.9
ShC, 10 mg/ml	7.6 ± 0.3	26.9 ± 0.5	79 ± 3
$\text{C}_{60}/\text{C}_{70}$, 0.1 mg/ml	6.9 ± 0.5	8.5 ± 0.3	6.6 ± 0.6
$\text{C}_{60}/\text{C}_{70}$, 0.1 mg/ml + 0.015 M NaCl	7.5 ± 0.2	14.2 ± 0.2	27.4 ± 0.8

The values of ΔE and ΔS (Table 1) suggest that the probe motion in frozen water and solutions of silica is the “slipping” by the rigid lattice, but in other cases this is the motion in viscous medium of surface water layers [12]. A kind of compensation effect reveals at that with rising the disperse phase concentration. That means a symbate increase of ΔE and ΔS , which is characteristic of the spin label motility in water-protein matrix [12].

It is seen from Figure 1 that the probe rotation frequency is sensibly constant within 255 K–245 K temperature range in dilute (0.1 mg/ml) dispersions of both fullerenes and ShC. It decreases on further lowering of temperature only. Such feature has not been observed for other samples. Similar kind of spin probe behavior is typical for phase transition. On the other hand, fullerites are known to undergo the first-kind phase transition from face-centered cubic lattice to simple cubic lattice on cooling at 260 K. Probably, some fullerene clusters reach the size of the new phase nuclei on cooling and undertake the phase transition. Heterogeneity of the sizes, hydration and structures result in widening of the phase transition temperature range. Analogous phenomenon characteristic of diluted aqueous dispersion of ShC is shown in Fig. 1. Moreover, heterogeneity is less pronounced and the temperature range of the phase transition is narrower for concentrated, less stable aqueous dispersions of ShC.

Parameter a_N is sensitive to the polarity of microenvironment due to the ability of spin probe nitroxide group to form H-bond with the surrounding water molecules. a_N decreases sharply just on water freezing in diluted fullerene and shungite dispersions (Figure 2). This suggests that the probe is preferentially localized in microenvironment where water molecules do not form H-bonds with nitroxide fragment. This can be water in hydrophobic pore (cavity) of nanocarbon cluster. Water in such pore can have specific cluster structure with almost undistorted H-bonds and reduced dissolvent capacity [10,13]. Water cluster lifetime in such pore may be comparable with the probe rotational correlation time. Pore dimensions are significant [13] as for large pores (50 nm pores in silica) the effect is not observed. At the same time, according to the SAXS and SANS data [14] the pores interacting with water in the fullerene and ShC clusters have dimensions of several to ten nm. Water cluster in the pore subjects to destructive effect of osmotic forces [13], e.g. on addition of electrolyte or on rising concentration of disperse phase (carbon nanoparticles). Considerable increase of a_N observed both in presence of NaCl in dispersion and on rising concentration of the dispersion, could be a result of such effect. Water attached at polar groups of the nanoparticle surface still remains unfrozen when water in hydrophobic pores has already frozen. The spin probe localized in that unfrozen water fraction retains relatively rapid motion down to 230 K and lower. The type of motion depends on solution composition and aggregating stability and determines the rotational activation parameters. Obviously the polar groups allocation and their hydration state are specific for each sample. This may be the reason for the registered differences.

Figure 3 presents variations of parameter ϵ that indicates the radical rotational anisotropy. Allowing for the sphericity of radical shape these variations are indicative of dominating contribution of the medium orienting properties caused by the radical and hydration water interaction potential. Although the values of ϵ always give the level of nonsphericity $N = \tau_{\perp}/\tau_{\parallel}$ close to 1, nevertheless the contribution of the orienting potential to the probe motility can be distinguished for dilute and concentrated nanocarbon dispersions.

Thus, carbon nanoparticles in low concentration dispersions that are stable to aggregation are likely to contain both hydrophobic cavities filled by long-living water clusters (nanophases) with a specific water structure and polar surface segments with water molecules, attached as separate fractions. Water structure in nonpolar cavities collapses first under the effect of electrolyte or at high dispersion concentration (low stability of dispersion to aggregation). Probably, just this water prevents contact interaction of the nanoparticles in cluster and their irreversible coagulation, while polar groups are exposed at outer carbon cluster surface and water attached by these groups

prevents cluster enlargement. As long as solutions of every carbon nanoparticles concentration coagulate rapidly after unfreezing, the initial water structure in the cavities does not reset.

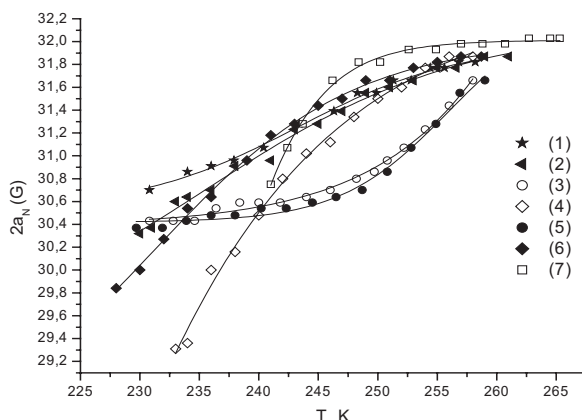


Figure 2. Temperature dependence of spin-probe EPR spectrum constant $2a_N$ for frozen water and dispersions of silica and carbon nanoparticles of different concentrations: (1) – frozen water; (2) – silica dispersion, 1 mg/ml; (3) – 0.1 mg/ml C_{60}/C_{70} ; (4) – 0.1 mg/ml $C_{60}/C_{70} + 0.015$ M NaCl; (5) – 0.1 mg/ml ShC; (6) – 1 mg/ml ShC; (7) – 10 mg/ml ShC (unstable dispersion).

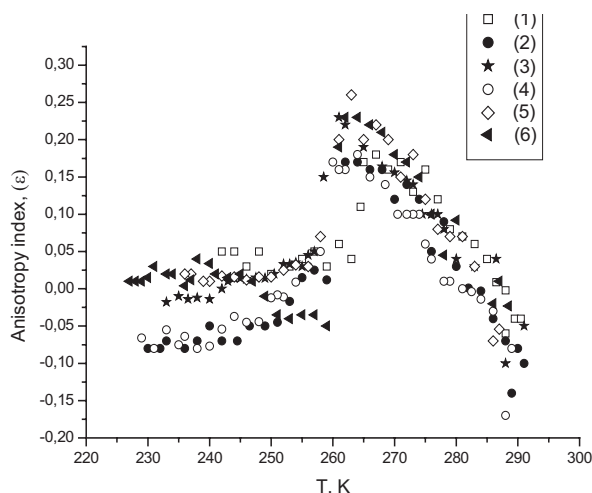


Figure 3. Temperature dependence of spin-probe EPR spectrum non-dimensional parameter ϵ for water and dispersions of silica, and carbon nanoparticles of different concentrations: (1) – 10 mg/ml ShC (unstable dispersion); (2) – 0.1 mg/ml ShC; (3) – water; (4) – 0.1 mg/ml C_{60}/C_{70} ; (5) – 0.1 mg/ml $C_{60}/C_{70} + 0.015$ M NaCl; (6) – 1 mg/ml silica.

4. Conclusions

Separate fractions (nanophases) of near-surface water attached probably by hydrophobic surface segments and hydrophobic pores as well as by polar chemical groups have been revealed in water fullerene and shungite carbon nanoparticles

dispersions using EPR spin probing of frozen solutions. Dynamic and structural properties of those phases are correlatable with the nanoparticles stability to aggregation.

Acknowledgements

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NANOSTRUCTURED CARBON MATERIALS BASED ON IR-PYROLIZED POLYACRYLONITRILE

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Abstract. IR pyrolysis of PAN and PAN based composites yields ordered graphite-like structure as well as several carbon nanostructures. Metal-carbon nanocomposites, in which the nanosized metal particles were introduced into the structure of carbon matrix in the course of IR pyrolysis of composite-precursor on the basis of PAN and metal (Gd, Pt, Ru, Re) compounds were prepared. The carbon phase of metal-carbon nanocomposites was shown to include different types of nanostructured carbon particles. Bamboo-like CNT were observed in the structure of pyrolyzed at 910 and 1000°C composite-precursor based on PAN and GdCl_3 . At $T=1200^\circ\text{C}$ the solid carbon spheres with diameter in the range of 50-360 nm and octahedral carbon particles with the size in the range of 300-350 nm were observed. These nanostructured particles consist of carbon only or they include Gd nanoparticles encapsulated in carbon shell. IR pyrolysis of composite-precursor based on PAN as well as H_2PtCl_6 and RuCl_3 or NH_4ReO_4 (Pt:Ru(Re)=10:1) allows the preparation of Pt-Ru and Pt-Re alloys nanoparticles with $2 < d < 13$ nm which are finely dispersed in carbon matrix.

Keywords: polyacrylonitrile, IR pyrolysis, graphite, carbon nanotubes, nanostructured carbon, transmission electron microscopy

1. Introduction

All-increasing interest of researchers in nanostructured carbon materials during over a decades is prompted by wide range of their potential use, for example, in nanoelectronics, fuel cells, hydrogen accumulators, reinforcing and membrane materials, thermal insulators, carriers for heterogeneous and electrocatalysts, labrificant additives etc. The great variety of nanostructured carbon materials has been discovered and studied such as fullerenes, multi-walled carbon nanotubes, single-walled carbon nanotubes, hollow and solid carbon nanospheres, carbon nanonions, single-walled carbon nanohorns and their metal included forms. Various preparation routes have been used to realize these carbon nanostructures, such as arc discharge, submerged arc in cold water or liquid nitrogen, plasma enhance chemical vapor deposition, thermal catalytic pyrolysis of hydrocarbon gases, as well as polymer precursor such as polyacrylonitrile (PAN), copolymer acrylonitrile with methylmethacrylate, polytetrafluoroethylene, chlorination of ferrocene and co-pyrolysis of C_2Cl_4 with ferrocene [1-7].

This study shows the possibilities and specific feature of IR-pyrolysis for the formation of nanostructured carbon. In such way PAN, thermal transformations of which have been studied in detail [8-11], was chosen as the precursor for preparation of nanostructured carbon materials by carbonization of PAN and its composites with gadolinium chloride under non-coherent IR radiation. Specific action of IR-radiation on vibrational energy of PAN bands macromolecules allows one to decrease extremely time treatment and as a result to make simple, low energy and cost-effective pyrolytic method.

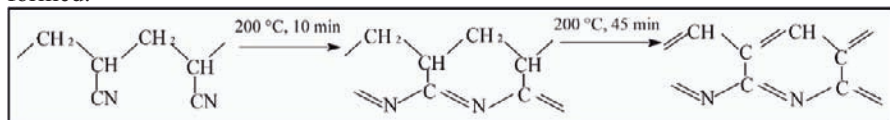
In this work chemical and structural transformation of pAN in dependence of IR radiation intensity and peculiarities of formation of metal-carbon nanocomposites are considered.

2. Experimental

Under IR radiation PAN samples undergo intense chemical and structural transformations. X-ray diffractogram of initial PAN has two reflexes of crystalline phase ($d_1=5.30$ Å, $d_2=3.06$ Å) and two wide maximums of amorphous phase ($d_3=3.43$ Å, $d_4=2.45$ Å). These parameters correspond to hexagonal packing of macromolecules [12, 13]. Ratio of crystalline and amorphous phases in polymer is 1:1. At this, the average size of domains of coherent scattering of crystallites is $L_c=95$ Å. At the temperature increase to 140°C the ratio of crystalline and amorphous phases does not change, while L_c increases to 110 Å. At $T=175^\circ\text{C}$ $L_c=135$ Å.

Heating of the sample to $T=200^\circ\text{C}$ gives start to chemical transformations of PAN, in the first place the reaction of cyclization of nitrile groups with formation of the system of conjugated $\text{C}=\text{N}$ double bonds. Specific effect of IR radiation on the vibrational energy of bonds of PAN macromolecule results in chemical and structural transformations of PAN proceeding at lesser intensities and during shorter times than under the conditions of common heating procedures. Thus, while cyclization of nitrile groups by common heating proceeds at $T=220^\circ\text{C}$ for 16 h [9], it takes just 15 min at $T=200^\circ\text{C}$ for the proposed method using IR radiation. It is important to note that the intensity of IR radiation was controlled by the temperature of the sample, measured by a chromel-coppel thermocouple in quartz tube placed directly under the sample. Controlling unit provided the changes in intensity of IR radiation at a given computer program. Temperature of the sample was maintained within 0.25°C .

The system of conjugated $\text{C}=\text{C}$ double bonds was shown to form when the duration of annealing at $T=200^\circ\text{C}$ is prolonged to 45 min. As a result, ribbon-like cyclical structures consisting of the systems of conjugated $\text{C}=\text{C}$ and $\text{C}=\text{N}$ bonds are formed.



Destruction of preliminary structured PAN films under intense IR radiation in inert atmosphere during very short time (10 s – 2 min) leads to the intensification of carbonization processes with the formation of ordered carbon structures. Figure 1 shows Raman spectra of PAN films carbonized by IR radiation.

Raman spectrum (insert in Fig. 1) shows two bands at 1355 and 1584 cm^{-1} (D- and G-lines, respectively), which attest to the existence of domains with different degree of order in carbonized phase. For highly oriented pyrolytic graphite and large single crystal graphite only G-line in Raman spectra is allowed [14], while disordered or fine graphite crystallites show both D- and G-lines [15, 16]. The line at 1355 cm^{-1} is induced by disorder. In our case ordered domains, with all probability, are graphite-like structures, judging by the presence of the 1584 cm^{-1} band.

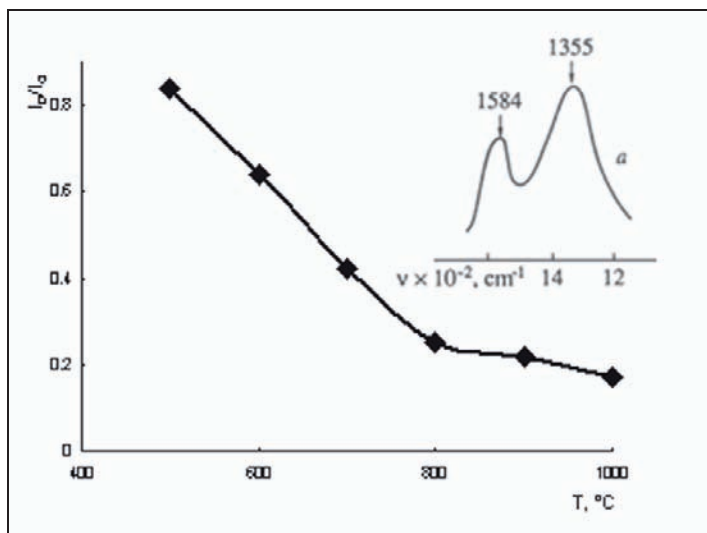


Figure 1. The IR radiation intensity dependence of ratio of Raman spectral intensity for bands 1355 cm^{-1} (D-line) and 1584 cm^{-1} G-line); insert (a): the Raman spectrum.

The rise in intensity of IR radiation does not change the placement of bands in Raman spectrum, only their intensities (Fig. 1). The intensity of the 1355 cm^{-1} band decreases, which attests to the formation of more ordered carbon structures.

Chemical reactions proceeding in the system under the conditions of IR pyrolysis result in the changes of PAN crystalline structure. X-ray phase analysis (XRPA) has shown that at $T > 200^\circ\text{C}$ in the course of formation of ordered carbon structures crystalline and amorphous phases of initial PAN disappear, while another amorphous carbon phases appear [12]:

1. Intermediate phase I, $d_{\text{max}} = 3.0\text{ \AA}$.
2. Graphite-like phase G, $d_{002} = 3.35\text{--}3.80\text{ \AA}$.
3. Polynaphtene phase N, $d = 4.70\text{ \AA}$.

The content of graphite-like phase was shown by XRPA to increase with an increase in intensity of IR annealing. Simultaneously there is a decrease in the content of polynaphtene and intermediate phases (Fig. 2). At 700°C IR pyrolyzed PAN (IRPAN) has a graphite-like structure only. It is amorphous due to the irregular shift of graphene layers in the plane ab and small size of domains where the crystallite scattering is coherent (L_c). Figure 3 shows the IR annealing intensity dependence of interlayer distance for graphite-like structure.

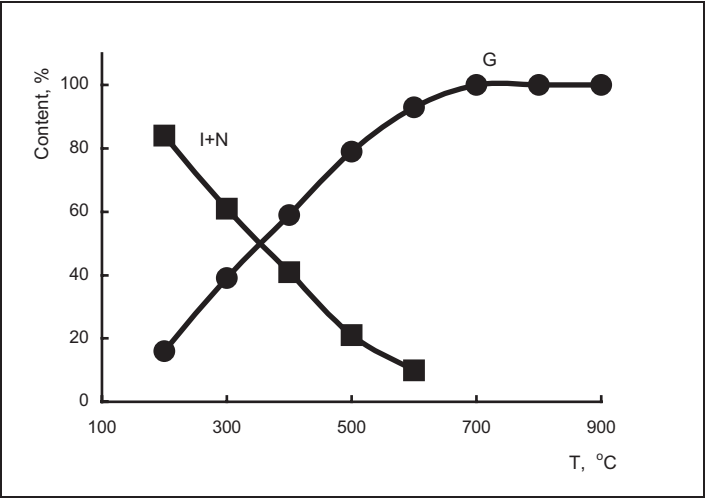


Figure 2. Content of I, G, N amorphous phases in IRPAN as function of IR annealing intensity.

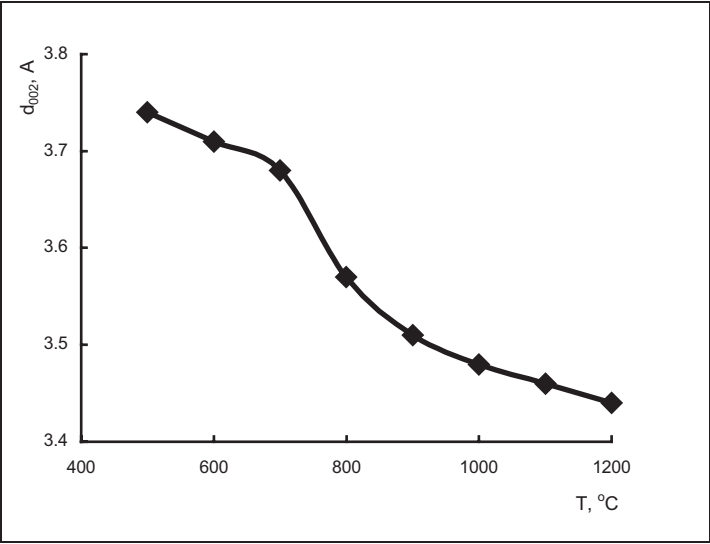


Figure 3. Interlayer distance d_{002} as a function of IR annealing intensity.

Crystallites sizes for graphite-like phase depending on IR radiation intensity are presented in the table 1.

TABLE 1. Crystallite size for graphite-like phase as a function of IR-radiation intensity

T, °C	400	500	600	700	800	900	1000	1100	1200
L_c , Å	18,2	21,3	24,9	27,8	29,7	31,6	35,6	36,9	37,2

These experimental data prove the fact that degree of order of graphite-like phase and crystallite size grow with the IR light intensity increase.

Obtained carbon materials are characterized by high stability at increased temperatures (temperature of testing should not exceed the temperature at which the material is produced, though), as well as in humid and aggressive (acidic and alkaline) media and under hyperbaric conditions.

Including into initial PAN solution metal compounds provides the formation of metal-carbon nanocomposites. The nanosized metal particles were introduced into the structured carbon matrix in the course of IR pyrolysis of composite-precursor on the basis of PAN and compounds of corresponding metals. In this way carbon composites containing nanosized Gd particles ($4 < d < 11$ nm) were prepared when $GdCl_3$ (20% mass.) was used as a component of composite-precursor. Efficient reduction of metal takes place in the course of IR pyrolysis of composite-precursor with participation of hydrogen, which is released in dehydrogenation of main polymeric chain of PAN.

The carbon phase of obtained metal-carbon nanocomposites was shown to contain different types of nanostructured carbon particles in parallel with main graphite-like structures. Bamboo-like carbon nanotubes (CNT) with 14-30 nm in their outer diameter were observed in structured carbon material when $GdCl_3$ was used as a component of composite-precursor (Fig. 4). In this case IR radiation intensity provides the heating of sample to 910 and 1000 °C.

In the course of IR pyrolysis, according to mass spectrometry and gas chromatography data, various gas products of destruction of PAN polymeric chain are present in the reaction chamber, including hydrocarbons such as ethylene and propylene [17, 18]. These hydrocarbons provide the carbon source. Catalytic decompositions of hydrocarbons at high intensity IR-radiation in the presence of metallic Gd leads to the formation of carbon nanostructures such as observed bamboo-like CNT. It is well known that Ni, Co Fe have conventionally been used widely as metallic catalysts for high temperature pyrolysis of hydrocarbons. Recently bimetallic components was shown to be more effective than single metals as catalysts. Especially transition metals with addition of rare-earth metals such as Y, Ce, Tb, La and Ho [19]. In this work catalytic activity of single metallic Gd in the IR-pyrolysis of hydrocarbons are found by us for the first time.

Thus, two processes take place at a time: carbonization and partially graphitization of PAN and catalytic pyrolysis of eliminated.

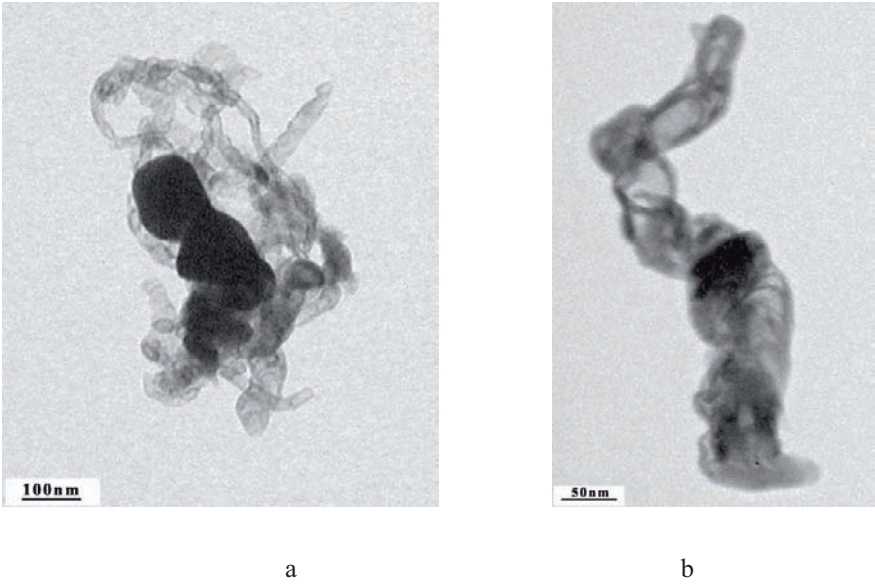


Figure 4. TEM image of nanocomposites IRPAN/Gd (a - $T=910^{\circ}\text{C}$, $t=1$ min, b – 1000°C , $t=1$ min).

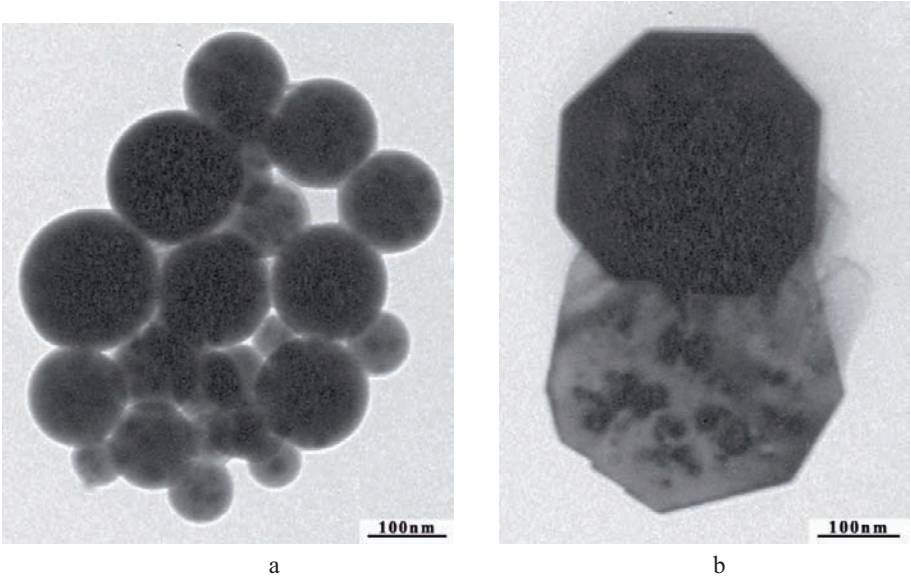


Figure 5. TEM images of nanocomposite IRPAN/Gd ($T=1200^{\circ}\text{C}$, $t=1$ min).

It is important to note that structural transformations of obtained bamboo-like CNT takes place while IR radiation intensity rises. At $T=1200^{\circ}\text{C}$ bamboo-like CNT are converted to solid carbon spheres with diameter in the range of 50-360 nm and octahedral carbon particles with the size in the range of 300-350 nm (Fig. 5). These nanostructured particles consist of carbon only or they contents Gd nanoparticles incapsulated in spherical or octahedral carbon particles. The mechanism of high temperature structural transformations of bamboo-like CNT still needs research.

Thus, the carbon phase of obtained metal-carbon nanocomposites represents in reality the carbon-carbon nanocomposite of main graphite-like structure with array of carbon nanostructures such as bamboo-like CNT, spherical or octahedral carbon nanoparticles.

Metal-carbon nanocomposites containing bimetallic nanosized Pt-Ru (Pt-Re) particles were prepared in the course of IR-pyrolysis composite-precursor containing PAN as well as H_2PtCl_6 and RuCl_3 (or NH_4ReO_4) in the ratio Pt:Ru (Re) = 10:1.

X-ray diffractogram pattern in the range $\theta=5-40^{\circ}$ shows the presence of wide peak of amorphous carbon phase and three narrow peaks of Pt. According to X-ray diffraction data, bimetallic nanosized particles are alloys with simple cubic lattice (parameter $a=3.888 \text{ \AA}$ for Pt-Ru and $a=3.899 \text{ \AA}$ for Pt-Re).

The decrease of the lattice parameter to these values from $a=3.923 \text{ \AA}$ for Pt [20] attests to formation of solid solutions of substitution. It is shown by TEM that bimetallic nanoparticles are finely dispersed in carbon matrix (Fig. 6).

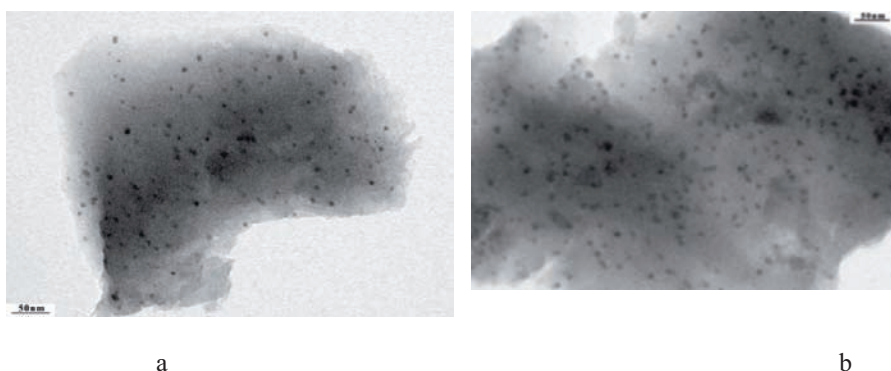


Figure 6. TEM image of nanocomposite IR-PAN/Pt-Ru (a) and IRPAN/Pt-Re (b).

Figure 7 depicts histograms of size distribution of bimetallic nanoparticles in carbon matrix. Nanoparticles finely dispersed in carbon matrix based on IRPAN are sized as $2 < d < 13 \text{ nm}$. In these nanocomposites $\sim 90\%$ Pt-Ru nanoparticles have a size as 4-7 nm and $>80\%$ Pt-Re nanoparticles have the size as 6-7 nm. This metal-carbon nanocomposites can be used as possible catalyst materials in fuel cells.

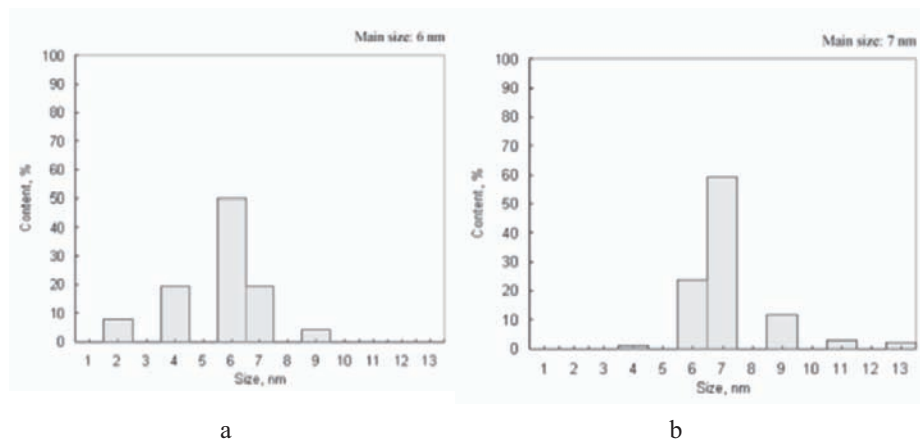


Figure 7. Histogram of size distribution of bimetallic Pt-Ru (a) and Pt-Re (b) nanoparticles in IRPAN ($T=700^{\circ}\text{C}$, $t=2$ min).

3. Conclusions

IR pyrolysis of PAN and PAN based composites yields ordered graphite-like structure as well as several carbon nanostructures, which were studied by means of Raman spectroscopy, XRD, including XRPA and TEM. The interlayer distance in graphite-like phase decreases and crystallite size grows with irradiation intensity increase.

Including into initial PAN solution metal compounds provides the formation of metal-carbon nanocomposites. The nanosized metal particles were introduced into the structure of carbon matrix in the course of IR pyrolysis of composite-precursor on the basis of PAN and compounds of corresponding metals (Gd, Pt, Ru, Re).

The carbon phase of obtained metal-carbon nanocomposites was shown to include different types of nanostructured carbon particles. Bamboo-like CNT with 14-30 nm in their outer diameter were observed in structured at $T=910-1000^{\circ}\text{C}$ carbon material when composite-precursor based on PAN and GdCl_3 was used. At $T=1200^{\circ}\text{C}$ the solid carbon spheres with diameter in the range of 50-360 nm and octahedral carbon particles with the size in the range of 300-350 nm were observed. These nanostructured particles consist of carbon only or they contain Gd nanoparticles encapsulated in spherical or octahedral carbon particles.

IR-pyrolysis of composite-precursor based on PAN as well as H_2PtCl_6 and RuCl_3 or NH_4ReO_4 (Pt:Ru(Re)=10:1) allows the preparation of Pt-Ru and Pt-Re alloys nanoparticles with $2 < d < 13$ nm which are finely dispersed in carbon matrix. Such metal-carbon nanocomposites can be used as the possible catalyst material in fuel cells.

Acknowledgements

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MOLECULAR HYDROGEN EVOLUTION: PHOTOCATALYTIC ACTIVITY OF MESOPOROUS TiO₂-CONTAINING METAL COMPOSITES

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Abstract. The photocatalytic reduction of metal cations ($M = Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Fe^{2+}, Ag^+, Pb^{2+}$) on the surface of mesoporous TiO₂, synthesized by sol-gel technique, was found to cause formation of nanostructured metal-semiconductor composites TiO₂/M.

The photocatalytic properties of nanostructured composites TiO₂/M at hydrogen evolution from water-alcohol mixtures were investigated. It was shown that photocatalytic activity of TiO₂/M samples increases with anatase content increase in the original mesoporous titania. The hydrogen evolution kinetics was thoroughly studied. It was shown that metal concentration in such systems (0.2-0.6 mass % in the case of TiO₂/Ni), is optimal and gives the maximum quantum yield of hydrogen (0.38 in the case of TiO₂/Ni).

Keywords: photocatalysis, hydrogen evolution, TiO₂, semiconductor nanoparticles, sol-gel synthesis, template synthesis, mesoporous materials, metal-semiconductor nanocomposites

1. Introduction

Review of literature concerning the photochemistry of inorganic compounds shows us that a substantial progress was achieved during the past two decades in understanding the photophysical and photochemical properties of nanometer semiconductor particles [1 - 4] and structurally organized semiconductor materials, including the nanostructured semiconductor films, mesoporous molecular sieves [5 - 10] etc., and, also in the elaboration of physical and chemical techniques for their synthesis and examination of their photocatalytic activity in various chemical and electrochemical redox-processes.

The high photocatalytic activity of TiO₂ in the transformations of various substrates, in conjunction with its stability towards photocorrosion, stimulated development of new routes for synthesis of titania with purposed texture, phase composition and, also, optical and electrophysical characteristics. Great progress in the understanding of the factors, determining the photocatalytic activity of titanium dioxide, the mechanisms of the photoprocesses, developing on the surface of TiO₂ crystals under their stationary and pulse irradiation has been achieved to this day [11-16]. It was shown that photocatalytic activity of TiO₂ is quite sensitive to the size, crystallinity and phase composition of TiO₂ particles, and anatase modification of TiO₂ being the most active in the photocatalytic processes. A number of approaches to TiO₂ utilization for solar energy conversion and

accumulation, purification of waste waters and air, development of bactericidal materials, etc., was developed [5, 11-13, 16, 17].

It should be noted that powdered TiO_2 -based photocatalysts, which are traditionally used in the majority of applications, have comparatively low specific surface area. A relatively low rate of reaction of the TiO_2 conduction band electrons in the absence of additional “dark-stage” catalysts, such as the noble metals (Pt [11, 12, 18-25], Rh [11, 12, 26], Pd [11, 13, 27], Ag [11, 28-30], Au [25, 31-33], Ir [27] etc.), deposited directly on the surface of a photocatalyst or on some inert substrate, hinders substantially the catalytic activity of TiO_2 materials.

In this connection, two ways are possible for further development of the photocatalytic systems, based on titanium dioxide. The first of them deals with the development of new techniques for preparation of the highly-porous (in particular, mesoporous) samples of titania with high specific surface area ($>100 \text{ m}^2\text{g}^{-1}$), freely accessible for substrates, as well as the ordered structure of pores and high anatase content. The second one involves the formation of composite (especially metal-semiconductor) materials, where the electronic contact between the composite components allows achievement of a high degree of primary separation of the photogenerated charge carriers and their involvement into redox-processes with adsorbed agents.

Here we report a technique of direct synthesis of the photocatalytically active mesoporous composites TiO_2/M ($\text{M} = \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}, \text{Zn}, \text{Ag}$ etc.) via photochemical reduction of the metal cations adsorbed on highly developed surface of a mesoporous titanium dioxide. The TiO_2/M composites were found to be efficient photocatalysts of hydrogen evolution from water-alcohol mixtures.

2. Experimental

Samples of mesoporous titanium dioxide were synthesized via sol-gel hydrolysis of Ti(IV) tetrabutoxide in 1-butanol by atmospheric moisture in the presence of a structure-directing template dibenzo-18-crown-6 ether. After completion of the sol-gel transformation and ageing of the precipitate, the mother liquor with the precipitate was exposed to hydrothermal treatment (HTT) at $100 - 175^\circ\text{C}$ for 24 h. Then, the precipitate was separated, dried, and calcinated on air at $350 - 500^\circ\text{C}$ for 4 hours.

The relative anatase content in the samples was calculated from the intensity of the X-ray diffraction band with maximum at $2\Theta = 25,4^\circ$ (the spectrum was registered by DRON-3M diffractometer, copper $K\alpha$ -line). Here, commercial TiO_2 P25 (Degussa Corp.), containing 75% of anatase [11, 12], was used as a reference standard. The average size of TiO_2 crystallites was estimated from the diffraction band of (101) lattice plane using Scherer's equation.

Parameters of the porous structure of titania samples (pores volume V_p , specific surface area S_{sp}) were calculated using BET theory [34] from the adsorption isotherms of methanol. The average pore diameter (D_p) values were estimated from the differential curves of pore size distribution.

Kinetics of the photocatalytic hydrogen evolution was studied in a temperature-controlled 10 ml glass reactor or in a parallel-sided optical glass cuvette. Suspensions were irradiated by the light of mercury high-pressure 1000 W

lamp in the range of 310-390 nm. The reaction mixtures were evacuated before irradiation.

TiO₂/M composites were synthesized in a photochemical reaction *in situ*, through irradiation of solutions, containing mesoporous TiO₂ powder and an aliquot of a metal salt solution (NiClO₄, Co(NO₃)₂, Fe(NO₃)₃, CuSO₄, AgNO₃, MnSO₄, Pb(CH₃COO)₂, CdCl₂, ZnCl₂). Molecular hydrogen concentration was determined by gas chromatography.

3. Results and Discussion

Synthesis of mesoporous TiO₂/M composites and their photocatalytic activity in hydrogen evolution. Hydrolysis of Ti(IV) tetrabutoxide with subsequent sol-gel transformation in the presence of dibenzo-18-crown-6 ether as a template yields amorphous titanium dioxide (Fig. 1). Calcination of the parental amorphous sample at 500 °C causes crystallization of TiO₂ and formation of a porous material with high specific surface area and a narrow pore size distribution with the average pore diameter 5.0 nm (Table 1, sample No. 2). Combination of the hydrothermal treatment (HTT) of TiO₂ samples at 100 - 175 °C with their subsequent calcination

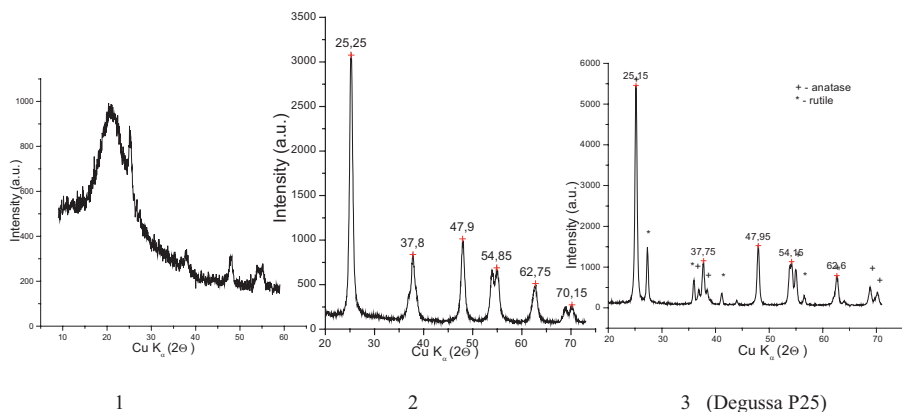


Figure 1. XRD pattern of titania powders synthesized under various conditions (**1**, **2**), as well as commercial TiO₂ Degussa P25 (**3**). The sample (**1**) was not exposed to the hydrothermal treatment (HTT) and was only calcinated at 500 °C, the sample (**2**) was exposed to HTT at 175 °C and then calcinated at 500 °C.

at 350 - 500 °C results in the crystallization of amorphous TiO₂ and formation of the mesoporous material having specific surface area over 100 m²·g⁻¹ and pore diameter $D_p > 7.0$ nm and consisting of small 10 nm TiO₂ crystallites. Increase of the HTT temperature, as well as the temperature of subsequent calcination of TiO₂ samples, leads to increase of the anatase content and the total volume and diameter of pores (samples No. 2-5). As can be seen from Table 1 and Fig. 1 sample 5 almost completely consists of anatase. It is well known that changing HTT conditions and subsequent calcinations of initially amorphous TiO₂ samples, we can improve the physical properties of the resulting anatase. So, this method is a way for perfection of the anatase-containing photocatalysts [35].

TABLE 1. Texture characteristics of mesoporous TiO₂ samples, synthesized at various conditions, and photocatalytic activity of corresponding TiO₂/Ni mesoporous composites with respect to hydrogen evolution

№	Sample	$t_{\text{HTT}},$ °C	$t_{\text{calc}},$ °C	$V_{\text{S}},$ cm ³ ·g ⁻¹	$S_{\text{sp}},$ m ² ·g ⁻¹	$D_{\text{p}},$ nm	$R,$ nm	$v_{\text{a}},$ %	γ
1	meso-TiO ₂	—	—	—	—	—	—	0	0
2	meso -TiO ₂	—	500	0.17	90	5.0	8.6	50	0.04
3	meso -TiO ₂	100	500	0.21	96	7.2	9.4	75	0.20
4	meso -TiO ₂	175	350	0.42	141	7.2	9.0	70	0.20
5	meso -TiO ₂	175	500	0.45	130	9.2	9.7	90	0.38
6	Degussa P25	—	—	—	50*	—	240*	75*	0.21

Notes: t_{HTT} is the temperature of hydrothermal treatment, t_{calc} is the calcination temperature, R is the average radius of TiO₂ particles, v_{a} is the anatase content in a sample (% of TiO₂ by mass), D_{p} is the average pores diameter, V_{S} is the total pores volume, S_{sp} is the specific surface area, and γ is the quantum yield of the evolved hydrogen.

Conditions of photochemical experiment: light intensity: $I_0 = 1.3 \cdot 10^{-6}$ einstein·min⁻¹; mass of the photocatalyst: 0.05 g; [Ni²⁺] = 0.5% of TiO₂ mass; temperature: 40 °C.

* From [3, 13].

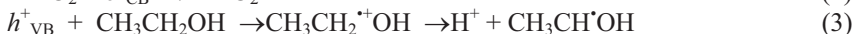
TABLE 2. Dependence of the quantum yield of photocatalytic molecular hydrogen evolution (γ) over TiO₂/M mesoporous composite on the metal nature

Photocatalyst	γ	a
TiO ₂	0	—
TiO ₂ /Cu	0.44	0.96
TiO ₂ /Ni	0.38	0.65
TiO ₂ /Co	0.06	0.60
TiO ₂ /Ag	0.03	0.73
TiO ₂ /Fe	0.02	0.76
TiO ₂ /Pb	0	1.36

Notes: Here, a is a constant in Tafel equation for hydrogen evolution overvoltage on the corresponding metal electrode (for alkaline media) [39]. TiO₂ was exposed to the hydrothermal treatment at 175 °C for 24 h and then calcinated at 500 °C for 4 h. The mass of the photocatalyst in the reactor was 0.05 g, reactor volume was 10 ml, the metal concentration was $4 \cdot 10^{-4}$ M, the ethanol:water ratio was 95:5, and the irradiation wavelength ranged within $\lambda_{\text{irr}} = 310 - 390$ nm.

At the irradiation of the mesoporous TiO₂ samples, dispersed in a water-alcohol mixture (typically containing 5 vol. % of H₂O and 95 vol. % of C₂H₅OH) without addition of any metal cations, we did not observe any molecular hydrogen evolution (Tables 2, 3). Suspension of the mesoporous titania becomes grey-blue in

the course of irradiation, which fact indicates that accumulation of Ti^{3+} cations in the bulk of the semiconductor takes place as a result of trapping of the photogenerated TiO_2 conduction band electrons [14, 36 - 38]:



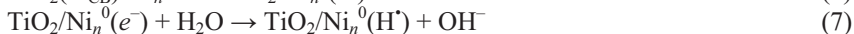
In turn, such a long-term accumulation of the trapped electrons indicates that the rate of withdrawal of the photogenerated electrons in reaction with water and ethanol in the absence of any additional electron transfer mediator proceeds with a small rate [11, 14].

Irradiation of mixtures containing the mesoporous titania and metal cations M^{2+} ($\text{M}^{2+} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{Fe}^{2+}, \text{Ag}^+, \text{Pb}^{2+}$), induces darkening of titania suspension and accumulation of molecular hydrogen in the reactor volume (with the exception of systems, containing Pb^{2+}). In the dark, we did not register any chemical reaction in such solutions. We supposed that samples darkening were induced by the photodeposition of the metals M^0 onto the surface of TiO_2 crystallites [28, 31].

The quantum yield of hydrogen, evolving in the presence of TiO_2/M^0 composites, varies from 0 to 0.44 in the consequence of M^0 : $\text{Pb} > \text{Fe} > \text{Ag} > \text{Co} > \text{Ni} > \text{Cu}$ (Table 2). The same dependence of photocatalytic H_2 evolution quantum yield from the nature of a surface-deposited metal was observed for commercial TiO_2 Degussa P25. It should be noted that the relative activity of metals in the investigated process does not correlate with the overvoltage value at hydrogen evolution on the corresponding metal electrode ($\text{Pb} \gg \text{Ag} > \text{Fe} > \text{Cu} > \text{Ni} \approx \text{Co}$) [39]. So, examination of the overvoltage dependence from the metal nature allows us to explain only the lack of the photocatalytic activity of TiO_2/Pb composite, since hydrogen evolution of lead-made electrode is the highest within the circle of the investigated metals. It does not also explain why copper has higher catalytic activity as compared with nickel and cobalt as well as substantial difference in the catalytic activities between nickel and cobalt (Table 2), having practically the same values of overvoltage at H_2 evolution [39]. Thus, catalytic activity of metal particles, formed on the surface of a semiconductor, is affected not only by the ability of the corresponding metal to accelerate some "dark" stages of the photocatalytic process, but also by a number of additional and still unknown factors, probably, such as the capability of metal cations to be adsorbed at specific sites on the surface of TiO_2 , size and surface state of the metal particles, electrophysical characteristics of the metal - semiconductor contact, etc.

Below we discuss the photochemical processes in the systems containing suspension of mesoporous TiO_2 and Ni^{2+} . Anatase conduction band potential at pH 7 amounts to -0.53 V versus NHE [11]; thus, photoreduction of Ni^{2+} ($E^0(\text{Ni}^{2+}/\text{Ni}^0) = -0.23$ V [40]) is thermodynamically favorable up to the practically total conversion of Ni^{2+} into Ni^0 ($E^0(\text{Ni}^{2+}/\text{Ni}^0) = -0.40$ V at 99% degree of Ni^{2+} photoreduction [40]). Investigations of metals (Ag [28-30], Au [31, 33], Pt [18, 22, 30], Pd [11], Cu , Hg [41] etc.) photoreduction at surfaces of porous samples and colloidal particles of TiO_2 shows, that in such systems metal is deposited on the semiconductor surface as separate particles of subnanometric – nanometric size. Such metal particles have ohmic contact with semiconductor surface [11, 24, 32] and developed electronic structure [24, 28-32]. So, we concluded that photocatalytic nickel(II) reduction takes place at irradiation of suspensions, containing mesoporous TiO_2 , Ni^{2+} and ethanol, this process resulting in the

formation of the metal-semiconductor composites TiO_2/Ni with close contact between the components. Comparison of the Fermi level of Ni^0 (-0.20 V versus NHE for bulk nickel [34]) with the potential of the bottom edge of TiO_2 conduction band allows us to assume the possibility of injection of the photogenerated TiO_2 electrons into Ni^0 nanoparticles, where they can participate in reduction of H^+ , water or ethanol:



On the Fig. 2 we present kinetic curves of hydrogen accumulation at irradiation of the water-ethanol mixtures, containing powdered mesoporous TiO_2 , preliminary exposed to HTT and calcination at 350 - 500 °C, as well as commercial TiO_2 Degussa P25, used without any pre-treatment. It could be seen from the Fig. 2, that the photoprocess proceeds with some acceleration at the initial stage of irradiation (~0.5 h). This phenomenon may be explained by the formation of nickel nanoparticles and their saturation with atomic and molecular hydrogen (reactions (4) – (8)).

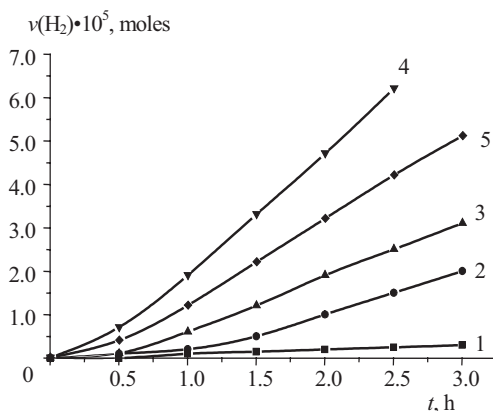


Figure 2. Kinetic curves of the photocatalytic evolution of molecular hydrogen from aqueous-alcoholic mixtures over TiO_2/Ni composites, derived from the samples of mesoporous TiO_2 , synthesized under various conditions (1 - 4), as well as commercial TiO_2 Degussa P25 (5). The sample (1) was not exposed to hydrothermal treatment (HTT) and was only calcinated at 500 °C, the sample (2) was exposed to HTT at 100 °C and then calcinated at 500 °C, the sample (3) was exposed to HTT at 175 °C and then calcinated at 350 °C, and the sample (4) was exposed to HTT at 175 °C and then calcinated at 500 °C. The photocatalyst mass: 0.05 g, reactor volume: 10 ml, ethanol:water ratio: 95:5, light intensity: $I_0 = 1.3 \cdot 10^{-6}$ einstein·min⁻¹, Ni^{2+} mass ratio 0.5 %.

Table 3 summarizes the values of H_2 quantum yield (γ) in systems, containing 0.5 mas. % of Ni^{2+} (per TiO_2 mass) and mesoporous titania. The table shows that our metal-semiconductor composites can catalyze hydrogen evolution with substantial quantum yields, their photocatalytic activity being much more

pronounced in the comparison with known-to-date mesoporous TiO_2 -based materials (see, for example, [9]). The photocatalytic activity of investigated mesostructured composites grows with an increase of the anatase content in the parental mesoporous material. Composites, produced from amorphous titanium dioxide (sample 1 in Table 3), proved to be inactive in the examined photoreaction. Samples 3 and 4 exhibit photocatalytic activity, comparable with that of commercial TiO_2 (Degussa P25). The maximal quantum yield of H_2 ($\gamma = 0.38$) was registered for the sample 5. As it can be seen from the Table 3, the photoactivity of this sample substantially exceeds that of Degussa P25 ($\gamma = 0.21$).

TABLE 3. Quantum yield of photocatalytic evolution of molecular hydrogen over TiO_2/Ni mesoporous composites (γ) in various conditions

No.	$m(\text{TiO}_2) \cdot 10^2$, g	$[\text{Ni}^{2+}]$, mass %	$[\text{H}_2\text{O}]$, M	γ
1	0.0	0.4	—	0
	2.0	0.4	—	0.12
	3.5	0.4	—	0.29
	5.0	0.4	—	0.38
	$5.0^{(1)}$	0.4	—	0.08
2	5.0	0.0	—	0
	5.0	0.05	—	0.30
	5.0	0.1	—	0.33
	5.0	0.2	—	0.38
	5.0	0.4	—	0.38
	5.0	0.6	—	0.38
	5.0	0.7	—	0.25
	5.0	0.8	—	0.10
	5.0	1.0	—	0.03
3	$5.0^{(2)}$	0.5	—	0.38
	5.0	0.5	—	0.38
	$5.0^{(3)}$	0.5	—	0.31
4	5.0	0.5	0	0.13
	5.0	0.5	0.5	0.17
	5.0	0.5	1.0	0.20
	5.0	0.5	2.0	0.20
	5.0	0.5	3.0	0.10
	5.0	0.5	5.0	0.04
	5.0	0.5	8.0	0.01

Notes: $m(\text{TiO}_2)$ – mass of a photocatalyst in reactor (reactor volume is 10 ml), $[\text{Ni}^{2+}]$ – mass of Ni^{2+} , as NiClO_4 in reacting mixture (in percents of the mass of a photocatalyst), $[\text{H}_2\text{O}]$ – molar concentration of water. Rows 1-3: TiO_2 sample was exposed after the synthesis to the hydrothermal treatment (HTT) at 175°C during 24 h and then calcinated at 500°C for 4 h. Row 4: the sample was exposed after the synthesis to the HTT at 175°C during 24 h and then calcinated at 350°C for 4 h. ⁽¹⁾ temperature of a reacting mixture is 20°C , in other cases – 40°C . ⁽²⁾ and ⁽³⁾ $I_0 = 0.6 \cdot 10^{-6}$ and $2.5 \cdot 10^{-6}$ einstein $\cdot\text{min}^{-1}$ correspondingly, in other cases $I_0 = 1.3 \cdot 10^{-6}$ einstein $\cdot\text{min}^{-1}$, irradiation wavelength range $\lambda_{\text{irr}} = 310 - 390$ nm.

Table 3 represents dependence of the quantum yield of hydrogen, evolving in a photocatalytic process over TiO_2/Ni composite with the maximal content of anatase

(sample 5 in Table 3), from conditions of the catalytic process. As the Table shows (see column 1), the quantum yield of the photoreaction increases with the photocatalyst mass increase and temperature elevation in the reacting mixture. Acceleration of the process of hydrogen evolution at temperature increase can be reasonably connected with facilitation of some "dark" thermal reactions of molecular hydrogen formation, such as atomic hydrogen diffusion, its recombination and desorption of H_2 from the surface of Ni catalyst (reaction (8)) [41].

Dependence of the quantum yield of hydrogen evolution versus Ni^{2+} concentration passes through the maximum (Table 3, column 2). The maximum rate of photoreaction over TiO_2/Ni composite can be achieved at Ni^{2+} content in the reacting mixture within 0.2 – 0.6 mass %. Investigation of the photocatalytic behavior of some metal-semiconductor composites, based on TiO_2 and a noble metal (Pt [11, 12, 18], Pd [11, 13], Rh [11, 12], Ag [11, 28] etc.) showed that the character of the photocatalytic process rate dependence versus metal concentration is general for these systems. Thus, for example, the maximum of the photocatalytic activity of the most widely studied TiO_2/Pt composites can be achieved at 0.5-1 mass % content of metal on the surface of the semiconductor [11, 12, 18]. Several possible reasons are claimed for a decrease of the quantum efficiency of the photochemical reactions at a relatively high content of metals, deposited on the surface of TiO_2 . Thus, for example, it can be caused by light filtration by the metal particles [11], or blocking of the active sites on TiO_2 surface by the deposited metal [18], or worsening of the catalytic properties of metal particles at their size increase (negative size effect) [11, 18, 20] etc. Examination of the dependence of γ versus the initial Ni^{2+} concentration allowed us to exclude the first and the second of the afore-mentioned mechanisms. In fact, the quantum yield of hydrogen evolution remains practically constant (0.38) at three-fold increase in the initial Ni^{2+} concentration (from 0.2 to 0.6 %, see Table 3, column 2), while filtration of light and blocking of the active surface sites by Ni^0 particles should cause substantial γ decrease in such conditions. Apparently, some alteration of the electronic and, possibly, surface structure of metal nanoparticles can occur after achievement of some critical size of Ni^0 nanoparticles, corresponding to 0.6 % of metal content, and it leads to passivation of the Ni^0 nanoparticles in the investigated photoprocess.

The rate of photocatalytic hydrogen evolution increases at light intensity (I_0) increase, while quantum yield of the photoreaction remains virtually constant in the range of $I_0 = (0.6 - 1.3) \cdot 10^{-6}$ einstein $\cdot$ min $^{-1}$ and slightly decreases at larger I_0 (Table 3, row 3). Reduction of γ at $I_0 > 1.3 \cdot 10^{-6}$ einstein $\cdot$ min $^{-1}$ was connected with an increase in the recombination rate of photogenerated in TiO_2 crystals charge carriers at high light intensities.

Dependency between γ values and water concentration in the reacting mixture (Table 3, column 4) was found to have an extremal character as well. Small rates of hydrogen photoevolution with pure ethanol as a donor of electrons is known to be common for systems with semiconducting photocatalysts of different nature (for example, CdS or CdS/CuS [42]), and most probably can be explained in terms of more favorable reductive decomposition of H_2O in comparison with CH_3CH_2OH [11, 42]. The γ value grows at an increase in the water content, apparently due to the involvement of H_2O molecules into the reaction with TiO_2 conduction band electrons, and reaches its maximum at $[H_2O] = 1.0-2.0$ M. Further augmentation of water concentration (taking into account the higher adsorption affinity of water to TiO_2 surface in comparison with ethanol [11, 12]) leads to almost complete saturation of the photocatalyst surface layer with water molecules and consequent impediment of the reaction between TiO_2 valence band holes and ethanol, increasing in that way the probability of electron-hole recombination.

4. Conclusions

We have studied photocatalytic properties of nanostructured metal-semiconductor composites, made from mesoporous samples of TiO_2 and a number of metals (Cu^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Fe^{2+} , Ag^+ , Zn^{2+} , Pb^{2+}) in hydrogen evolution from water-ethanol solutions. Correlations between the quantum yields of the photoreaction and various parameters of the reacting system (such as the metal nature and concentration, photocatalyst quantity, light intensity, temperature) have been found and discussed. It has been shown, that maximal quantum yield of hydrogen production ($\gamma = 0.44$) could be achieved in case of TiO_2/Cu composite.

Detailed examination of the photocatalytic activity of TiO_2/Ni samples has shown that the rate of the photocatalytic process grows at an increase in the anatase content increase in the original mesoporous TiO_2 samples, used for photochemical synthesis of TiO_2/Ni composite. This parameter, in turn, depends on the synthesis conditions of titanium dioxide, especially, on the temperature and duration of post-synthetic hydrothermal treatment and subsequent calcination. The photocatalytic activity of mesoporous TiO_2 samples, investigated in this work, has been found to be greater than that of the known-to-date photocatalysts, based on mesoporous titanium dioxide and commercial samples of TiO_2 .

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CHANGE OF CURIE TEMPERATURE AND EFFECTIVE EXCHANGE FIELDS IN FERRIMAGNETIC $R_2Fe_{14}B$ COMPOUNDS UPON HYDROGENATION

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Abstract. The magnetic properties (magnetic ordering temperature and magnetization) of the ferrimagnetic compounds $R_2Fe_{14}B$ ($R = Gd, Tb, Dy, Ho$ and Er) and their hydrides $R_2Fe_{14}BH_{2.5}$ were studied. It was found that incorporation of hydrogen into the crystal lattice of $R_2Fe_{14}B$ compounds substantially increases the Curie temperature and Fe-Fe exchange interactions. Hydrogenation does not practically change the intersublattice exchange field h_{21} and exchange field h_{22} within the R - sublattice. This effect can be understood as a result of the attendant changes in the unit cell volume and an electronic structure of these compounds.

Keywords: rare-earth compounds, hydride, magnetic ordering temperature, exchange field

1. Introduction

The insertion of light interstitial elements into the crystal lattice of $R_2Fe_{14}B$ (R – rare-earth and Y metal) intermetallic compounds results in a change of their magnetic properties (the Curie temperature, saturation magnetization, magnetic anisotropy and spin-reorientation transitions) [1-3]. The most dramatic changes are observed for the Curie temperature. The magnetic ordering temperature is governed by three kinds of exchange interactions: Fe-Fe, R-Fe and R-R. It is known that the exchange interaction between the iron atoms (Fe-Fe coupling) is stronger than the one between the iron and rare-earth ($R - Fe$ coupling) sublattices and exchange interaction within the rare-earth ($R - R$ coupling) sublattice in these compounds. The importance of R-Fe exchange interaction investigation is accounted by the fact that the effective exchange field of the iron sublattice is responsible for the magnetization level of the rare-earth sublattice. An appropriate level of the rare-earth ions magnetization is necessary to create the giant magnetic anisotropy in $R - Fe$ compounds. To obtain information about the R-Fe intersublattice interaction it is useful to compare the Curie temperatures of compounds containing magnetic and nonmagnetic R atoms. Subsequently, analyzing the Curie temperature in terms of the molecular-field model [4-7] one can calculate the exchange field h_{21} induced on the rare-earth sublattice by the iron magnetic moments sublattice.

The purpose of the work is to study the effects associated with the influence of interstitial hydrogen on the exchange interactions (Fe – Fe, R – Fe, R - R) in ferrimagnetic $R_2Fe_{14}B$ compounds (R = Gd, Tb, Dy, Ho and Er).

2. Experimental

High-purity rare-earth metals purified by vacuum distillation-sublimation (the content of basis metal is 99.956-99.983 at %), Armco iron, and Fe-(1.2-1.5 wt %)B alloying composition were used as starting components. The single-phase samples of $R_2Fe_{14}B$ (R = Gd, Tb, Dy, Ho, Er and Y) composition were obtained by using the threefold arc melting in a purified helium atmosphere and rather rapid cooling. The samples placed in evacuated quartz ampoules were annealed at 700°C for 200 h. The phase composition of the samples was determined by X-ray diffraction analysis using a DRON-3M diffractometer. The elemental composition of the alloys was controlled by EDAX that allows the simultaneous study of the microstructure of the alloys.

The samples were subjected to hydrogenation using the high-purity hydrogen (containing no more than 10^{-3} - 10^{-4} % impurities) to the H/R ratio 2.5. Such hydrogen content allowed us to save the single-crystal form of the grains. The hydrogenation and EDAX measurements were performed at the Institute of Low Temperature and Structural Research, PAS (Wroclaw, Poland).

Thermomagnetic analysis was used to determine the magnetic ordering temperature (T_C) of the host compounds and their hydrides. The magnetization of $R_2Fe_{14}B$ and $R_2Fe_{14}BH_{2.5}$ was measured in the 300 – 800 K temperature region in magnetic fields up to 13 kOe using a pendulum magnetometer. The magnetization measurements at $T = 4.2$ K were performed using a standard SQUID-magnetometer.

3. Results and discussion

The X-ray studies of initial and hydrogenated compounds $R_2Fe_{14}BH_x$ ($x = 0$; 2.5) allowed us to obtain the crystal unit cell parameters (Table 1) which agree well with literature data [1, 2]. It is seen that the hydrogenation leads to an increase of the unit cell volume. The data for $Lu_2Fe_{14}B$ and $Lu_2Fe_{14}BH_{2.5}$ compounds have been published recently in Ref. [8].

It was found that the hydrogenation affects the saturation magnetization (σ_s), rising its value (Table 1). A substantial increase of the magnetic ordering temperature upon hydrogenation (about 30 K per hydrogen atom) was also observed (Table 2). The Curie temperatures were determined as the temperatures where the $|d\sigma/dT|$ has a maximum within the ferro - paramagnetic transition. The $\sigma(H)$ curves measured at temperatures near T_C were processed by Belov - Arrotte procedure. Here, the Curie temperature is defined as the temperature where the H/σ vs. σ^2 straight line passes through the origin. The values of T_C obtained according to this procedure practically coincide (within 2 K) with the data derived using the former method.

The Curie temperatures of $R_2Fe_{14}B$ compounds can be calculated from the expression:

$$T_C = \frac{1}{2}(\Theta_0 + \Theta_R) + \frac{1}{2}\sqrt{(\Theta_0 + \Theta_R)^2 + 4(\Theta_{RFe}^2 - \Theta_0\Theta_R)}. \quad (1)$$

TABLE 1. Crystallographic and magnetic characteristics of $R_2Fe_{14}B$ compounds and their hydrides $R_2Fe_{14}BH_x$ ($R = Y, Gd, Tb, Dy, Ho, Er, Lu$ and $x = 0; 2.5$)

Compound	a(Å)	c(Å)	V(Å ³)	$\Delta V/V(\%)$	σ_s (emu/g) T = 4.2 K
Y ₂ Fe ₁₄ B	8.75	12.04	921.81	-	177
Y ₂ Fe ₁₄ BH _{2.5}	8.85	12.10	947.70	2.81	187
Gd ₂ Fe ₁₄ B	8.76	12.00	920.85	-	93
Gd ₂ Fe ₁₄ BH _{2.5}	8.84	12.09	944.78	2.6	103
Tb ₂ Fe ₁₄ B	8.74	11.98	915.12	-	62
Tb ₂ Fe ₁₄ BH _{2.5}	8.83	12.07	941.08	2.84	70
Dy ₂ Fe ₁₄ B	8.73	11.97	912.27	-	58
Dy ₂ Fe ₁₄ BH _{2.5}	8.82	12.06	938.18	2.84	65
Ho ₂ Fe ₁₄ B	8.73	11.96	911.51	-	59
Ho ₂ Fe ₁₄ BH _{2.3}	8.82	12.05	937.40	2.84	68
Er ₂ Fe ₁₄ B	8.72	11.94	907.90	-	69
Er ₂ Fe ₁₄ BH _{2.5}	8.81	12.02	932.95	2.76	80
Lu ₂ Fe ₁₄ B	8.71	11.88	901.1	-	139
Lu ₂ Fe ₁₄ BH _{2.5}	8.77	11.96	919.2	2.01	148

TABLE 2. Effective exchange fields h_{11} (within the Fe-sublattice), h_{21} (affecting the R-sublattice) and h_{22} (within the R-sublattice) for compounds $R_2Fe_{14}BH_x$ ($R = Y, Gd, Tb, Dy, Ho, Er, Lu$ and $x = 0; 2.5$)

Compounds	T _C , K	h_{21} , 10 ⁶ Oe	h_{11} , 10 ⁶ Oe	h_{22} , 10 ⁶ Oe	Compounds	T _C , K	h_{21} , 10 ⁶ Oe	h_{11} , 10 ⁶ Oe	h_{22} , 10 ⁶ Oe
Y ₂ Fe ₁₄ B	565	-	6.26	-	Y ₂ Fe ₁₄ BH _{2.5}	650	-	6.81	-
Gd ₂ Fe ₁₄ B	661	1.14	-	0.401	Gd ₂ Fe ₁₄ BH _{2.5}	746	1.12	-	0.407
Tb ₂ Fe ₁₄ B	620	1.11	-	0.401	Tb ₂ Fe ₁₄ BH _{2.5}	705	1.10	-	0.407
Dy ₂ Fe ₁₄ B	598	1.14	-	0.401	Dy ₂ Fe ₁₄ BH _{2.5}	683	1.13	-	0.407
Ho ₂ Fe ₁₄ B	573	1.09	-	0.401	Ho ₂ Fe ₁₄ BH _{2.5}	658	1.09	-	0.407
Er ₂ Fe ₁₄ B	554	1.00	-	0.401	Er ₂ Fe ₁₄ BH _{2.5}	639	1.01	-	0.407
Lu ₂ Fe ₁₄ B	535	-	5.93	-	Lu ₂ Fe ₁₄ BH _{2.5}	620	-	6.50	-

This relation followed from the classical Neel's theory of ferrimagnetism [9] was derived and analyzed earlier in [10, 11]. $\Theta_0, \Theta_R, \Theta_{RFe}$ - represent the contributions into T_C due to the Fe-Fe, R-R, R-Fe exchange interactions, respectively.

Having recalled the expressions for the Curie constants C_1 and C_2 :

$$C_1 = \frac{N_1 \mu_B^2 g_1 J_1 (J_1 + 1)}{3k_B}, \quad C_2 = \frac{N_2 \mu_B^2 g_2^2 J_2 (J_2 + 1)}{3k_B} \quad (2)$$

where J_1 and J_2 are the total angular momentum of Fe and R atoms, respectively. One can find the appropriate contributions to the Curie temperature as follows:

$$\Theta_0 = C_1 \frac{2h_{11}}{N_1 \mu_B} \frac{(g_1 - 1)^2}{g_1^2}, \quad (3)$$

$$\Theta_{RFe}^2 = A_1 h_{21}^2 G, \quad (4)$$

$$\Theta_R = A_2 G, \quad (5)$$

where the coefficients A_1 and A_2 are:

$$A_1 = \frac{4\mu_B^2}{9k_B^2} S_1 (S_1 + 1), \quad (6)$$

$$A_2 = \frac{2Z_{22}A_{22}}{3k_B} = \frac{2\mu_B}{3k_B} h_{22}. \quad (7)$$

Here N_1 and N_2 are the numbers of Fe and R atoms per mole, respectively; g_1 and g_2 are the corresponding Lande factors; G – is de Gennes factor; h_{11} , h_{22} and h_{21} – effective exchange fields, S_1 is spin of Fe ions, Z_{22} is the number of R neighbors of each R atom, A_{22} – is the exchange interaction integral of R atom with R neighbors.

The Curie temperature of $R_2Fe_{14}B$ compound with a nonmagnetic rare-earth element ($\Theta_R = 0$, $\Theta_{RFe} = 0$) can be determined from the condition:

$$T_{C0} = \Theta_0. \quad (8)$$

After squaring Eq. (1) and making some algebraic transformations, we obtain the following expression:

$$\frac{T_C \Delta T_C}{G} = A_1 h_{21}^2 + A_2 \Delta T_C, \quad (9)$$

where

$$\Delta T_C = T_C - T_{C0} \quad (10)$$

The obvious merit of Eq. (9) is the explicit dependence of the Curie temperature on the de Gennes factor and the possibility to estimate the exchange field h_{21} from the Fe sublattice acting on the rare-earth ions.

Figure 1 displays the plots of the $T_C \Delta T_C / G$ quantity as a function of ΔT_C derived from our experimental results for the $R_2Fe_{14}B$ compounds and their hydrides. The data for the lutetium compounds ($T_{C0} = 535$ K for $Lu_2Fe_{14}B$ and $T_{C0} = 620$ K for $Lu_2Fe_{14}BH_{2.5}$) have been adopted as a T_{C0} . It is known that the 4f electron shell of the Lu^{3+} ($4f^{14}$) - ion has no magnetic moment. Therefore, in our case, the Lu compound models the iron sublattice magnetization for the whole series of R-Fe compounds under consideration.

The experimental values in Fig. 1 fit well to a linear relation $\frac{T_C \Delta T_C}{G} = f(\Delta T_C)$ given by Eq. (1). The intercept of these straight lines with the vertical axis and their

slopes of $\frac{T_C \Delta T_C}{G} = f(\Delta T_C)$ permit one to determine the h_{21} and A_2 (and h_{22} from Eq. (7)) parameters.

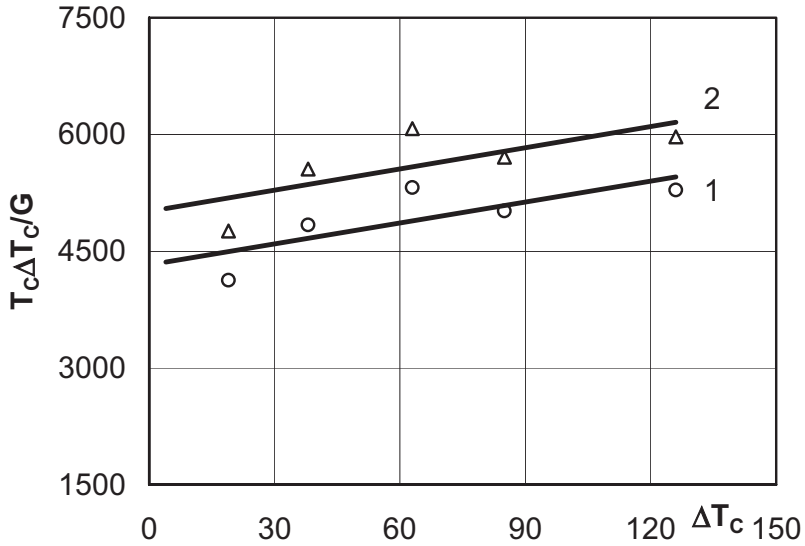


Figure 1. $\frac{T_C \Delta T_C}{G}$ plotted vs. ΔT_C for $R_2Fe_{14}B$ (1) and $R_2Fe_{14}BH_{2.5}$ (2).

The calculation results for $R_2Fe_{14}B$ and their hydrides are summed up in Table 2. The analysis of the obtained results allows us to conclude the following:

- 1) Introduction of hydrogen atoms into the crystal lattice of $R_2Fe_{14}B$ compounds leads to increase of the Fe-Fe exchange interactions.
- 2) On the other hand, the hydrogenation causes the weakening of R-Fe exchange interactions for Gd, Tb and Dy compounds; the R-Fe exchange interactions are virtually unchanged for compounds with Ho and Er.
- 3) Hydrogenation does not practically change the exchange field h_{22} within the R - sublattice.

According to the spin fluctuations theory, the Curie temperature of the band ferromagnets is inversely proportional to the density of states in the subbands near the Fermi level, $N\uparrow(E_F)$ and $N\downarrow(E_F)$. The increase of the lattice parameters after the hydrogen atoms incorporation to the lattice induces the decrease of the degree of wave-function hybridization between the $3d$ -electrons of Fe atoms and $5d$ -electrons of rare-earth metal atoms. This in turn entails the decrease of density of states in both zones $N\uparrow(E_F)$ and $N\downarrow(E_F)$.

Furthermore, the insertion of hydrogen atoms doesn't practically change the intersublattice exchange interactions in $R_2Fe_{14}B$ compounds. To explain this result a number of factors should be taken into account: (i) the volume effect under the hydrogen atoms incorporation, which increases the Fe-Fe and R-Fe interatomic distances, (ii) the enhancement of magnetism of the iron sublattice, (iii) the elastic

strains created by the incorporated hydrogen atoms, (iv) the change in the local electron concentration around the interstitial atom (the chemical effect). All these effects could compensate each other and cause the intersublattice exchange interaction to be almost invariable.

4. Conclusions

Thus, we established that incorporation of hydrogen atoms into the crystal lattice of $R_2Fe_{14}B$ compounds leads to a substantial increase of the Curie temperature T_C , and to enhancement of the Fe–Fe exchange interactions. The R-Fe and R-R exchange interactions remain unchanged. Some of these phenomena can be explained as a result of the unit cell volume and an electronic structure of the compounds changes.

Acknowledgements

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MAGNETIC PROPERTIES OF SOME $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ HYDRIDES

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Abstract. Magnetic properties of intermetallic compound $\text{Er}_2\text{Fe}_{14}\text{B}$ and its hydrides $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ have been investigated. Measurements of the temperature dependencies of magnetization have been performed with the permanent control of the hydrogen content in the investigated samples. The dependencies of Curie (T_C) and spin-reorientation transition (T_{SR}) temperatures on the hydrogen pressure and concentration of the inserted hydrogen atoms in the crystal lattice have been determined. Reasoning from the experimental data for T_{SR} , T_C and exchange parameters, the crystal field parameters and their change with the concentration of the inserted hydrogen atoms have been calculated.

Keywords: rare-earth compounds, hydride, magnetic ordering temperature, spin-reorientation transition

1. Introduction

The intrinsic magnetic properties of the $\text{Er}_2\text{Fe}_{14}\text{B}$ intermetallic compound have been previously investigated [1]. According to the literature data [1, 2] the magnetic ordering temperature of this compound is $T_C = 554$ K. $\text{Er}_2\text{Fe}_{14}\text{B}$ exhibits one successive spin reorientation transition (SRT) at about 325 - 327 K.

The $\text{R}_2\text{Fe}_{14}\text{B}$ (R - rare-earth) compounds absorb a copious amount of hydrogen readily and form stable hydrides at room temperature [2-4]. The changes in the magnetic characteristics of these compounds which occur due to the hydrogen absorption are of great fundamental and technological interest.

The permanent control of the hydrogen content in investigated compounds during the measurements plays an important role when the influence of hydrogen on magnetic properties (especially at high temperatures) of intermetallic compounds is under study. The magnetization measurements under fixed hydrogen pressure in the temperature interval including T_C for the RFe_{11}Ti compounds have been performed earlier [5-7]. Performing of similar investigations for other types of intermetallic compounds, particularly $\text{R}_2\text{Fe}_{14}\text{B}$, is of great interest.

The aim of this work is to study the effect of hydrogenation on the magnetic phase transitions (Curie and spin-reorientation transition temperatures) in the $\text{Er}_2\text{Fe}_{14}\text{B}$ compound using the magnetization measurements with continuous control of the hydrogen content in the examined sample.

2. Experimental details

As starting materials we used the rare-earth metal (Er) that has been purified by sublimation, Armco iron, and Fe-B alloying composition. An original furnace has been designed and purification regimes were developed at Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences [8, 9]. The purification process was realized in a resistor furnace at residual pressure of $1.33 \cdot (10^{-8} - 10^{-9})$ atm using a graphite heater. A rare-earth metal placed in a tantalum crucible has been evaporated at temperature 150°C below its melting temperature and subsequently deposited on a water-cooled copper condenser in the form of a druse of small crystals grown together. The impurity composition of metals has been determined using a laser mass spectrometry. The purified metal (of 99.956–99.983 wt % purity) is characterized by low contents of metallic and interstitial elements, in particular, oxygen, which concentration as a result of the purification has been decreased by two orders of magnitude.

The $\text{Er}_2\text{Fe}_{14}\text{B}$ compounds have been prepared by arc melting in a high-purity helium atmosphere using a water-cooled copper bottom and a non-consumable tungsten electrode. Specific regime of rapid cooling has been used (that allows to exclude the primary crystallization of $\alpha\text{-Fe}$). At the same time, the solidification should not be very rapid to allow the occurrence of a peritectic reaction for the formation of principal magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase in the arc furnace. As a result, we have obtained practically single-phase compounds with well-defined directional structure. After melting the as-cast samples were wrapped in a tantalum foil, sealed in quartz tubes and annealed in argon atmosphere at 700°C for 200 h. The phase composition of the compounds has been determined by the X-ray diffraction analysis, using a DRON-3M diffractometer. The quantity of impurity phase ($\alpha\text{-Fe}$) has been estimated by both X-ray and thermomagnetic analysis (TMA) to be about 3%.

The magnetization measurements have been carried out using an apparatus for magnetic measurements, constructed on the principle of a vibrating-sample magnetometer in the temperature range of 300–700 K in permanent magnetic fields up to 12 kOe under gas pressure up to 12 atm.

During the measurements of the temperature dependence of magnetization ($\sigma(T)$), the sample has been placed in a chamber with constant hydrogen pressure. In order to determine the hydrogen concentration x in the sample at any temperature ($x(T)$), a volumetric type experimental set-up [10, 11] has been used to study the hydrogen absorption-desorption properties at hydrogen pressures up to 4 atm in the temperature range from 300 to 700 K.

3. Results and Discussion

The investigations of magnetic properties of hydrides $\text{Er}_2\text{Fe}_{14}\text{BH}_x$, that have been carried out previously have not taken into account the hydrogen loss in the sample with temperature increase. We have used an apparatus that has allowed to measure the magnetic properties of the sample at high temperatures in hydrogen atmosphere with pressure control.

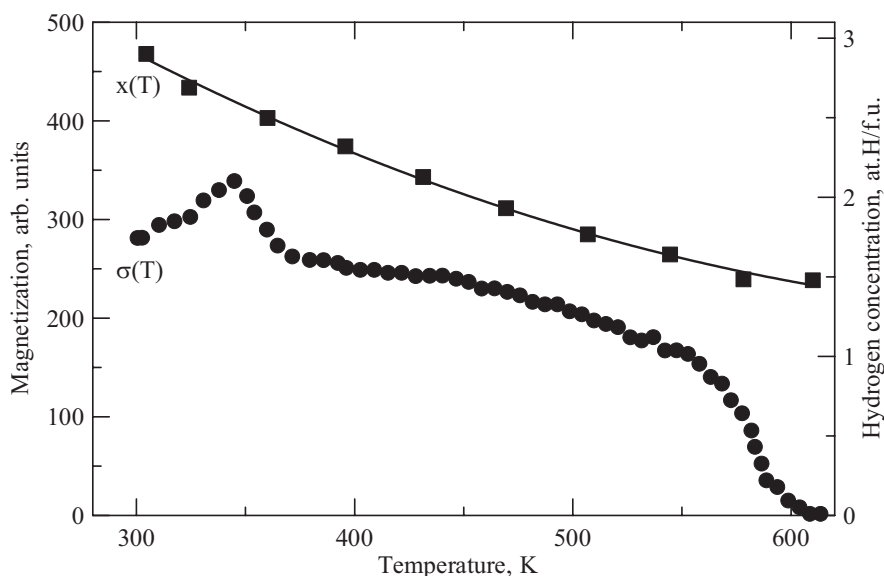


Figure 1. Temperature dependencies of magnetization and hydrogen concentration for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ at hydrogen pressure $P = 2.5$ atm.

Figure 1 shows the representative curves $\sigma(T, H=1.6 \text{ kOe})$ and $x(T)$ (allows to determine the hydrogen concentration at any temperature) at $P = 2.5$ atm in the chamber with the $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ sample.

A slump of magnetization at $T \sim 585 \text{ K}$ under sample heating corresponds to the Curie temperature of this compound and the SRT peak on the $\sigma(T)$ curve is observed at $T_{\text{SR}} = 345 \text{ K}$.

The experimentally determined dependence of T_C on the hydrogen pressure in the chamber with the investigated sample is presented in Fig. 2. As it is shown in Fig. 2, the Curie temperature strongly depends on the hydrogen pressure: in the interval $0 < P < 1$ atm, the increase of hydrogen pressure leads to the fast increase of T_C from $T_C = 552 \text{ K}$ to $T_C = 580 \text{ K}$. Further increase of T_C slows down, at $P > 1.5$ atm the $T_C(P)$ dependence is almost linear and at $P = 4$ atm the Curie temperature reaches the value of 586 K .

Figure 3 shows the dependence of the spin-reorientation transition temperature on the hydrogen pressure. As one can see from the figure, there is a correlation between the $T_C(P)$ and $T_{\text{SR}}(P)$ curves. It should be mentioned that, according to our results, the spin-reorientation transition temperature in the $\text{Er}_2\text{Fe}_{14}\text{B}$ compound ($T_{\text{SR}} = 307 \text{ K}$) is considerably less (by 20 K) than in literature data [2]. This fact can be explained as follows. By virtue of the fact that these compounds could absorb hydrogen at room temperature and atmosphere pressure, the host $\text{Er}_2\text{Fe}_{14}\text{B}$ samples [2] have contained some amount of hydrogen in advance.

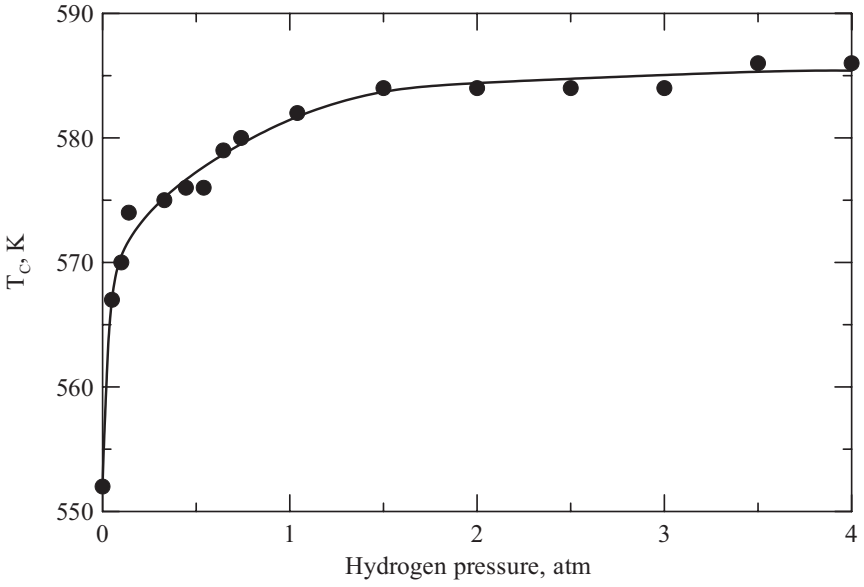


Figure 2. The dependence of Curie temperature on the hydrogen pressure for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$.

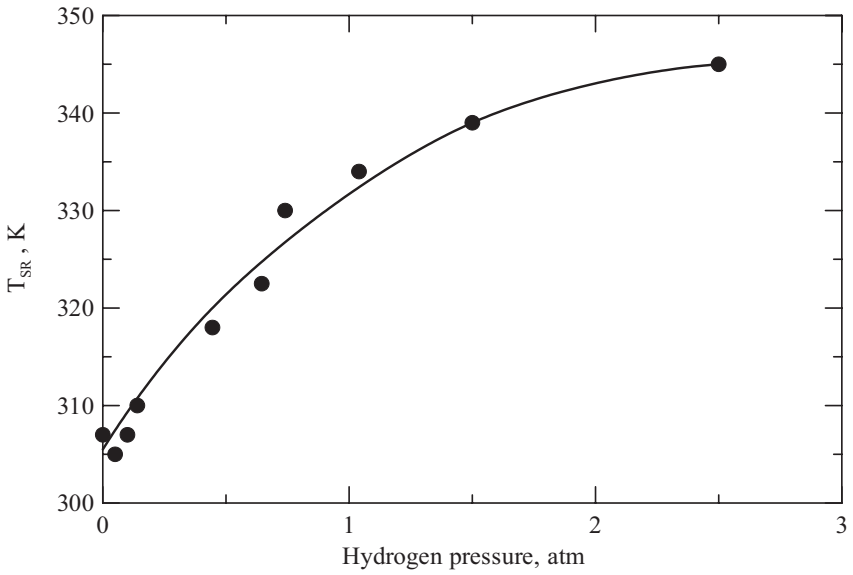


Figure 3. The dependence of spin-reorientation transition temperature on the hydrogen pressure for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$.

The dependencies of T_C and T_{SR} on the hydrogen concentration x , derived from the isobars data are presented in the Fig. 4 and 5, respectively. We emphasize that the $T_C(x)$ dependence is characterized by a linear rise up to the $x \sim 1$ at.H/f.u.

concentrations. This behavior is evolved from the linear dependence of the integral of exchange interactions on the unit cell volume. Probably, in this interval of hydrogen concentrations, the linear increase of the unit cell volume occurs under filling of the tetrahedral holes by the incorporated atoms. At higher concentrations ($x > 1$), Curie temperature growth impairs that is seemingly connected to the filling of the other type of tetrahedral holes by the hydrogen atoms and furthermore, it is a possible consequence of the valence bond filling by additional electrons from the hydrogen atoms incorporated.

As it follows from Fig. 5, the T_{SR} is nearly constant at the hydrogen atoms concentrations of $x < 1.5$. At concentrations $x \geq 1.6$ a sharp linear rise of $T_{\text{SR}}(x)$ curve is observed. This effect differs from the $T_{\text{C}}(x)$ dependence.

A constancy of T_{SR} up to the $x < 1.6$ concentrations may be explained by the fact that there is only a change of the unit cell volume in this interval of concentrations. It is well known, that the anisotropy constant is almost independent of the unit cell volume, but strongly depends on the axial relation of the crystal lattice parameters c/a . Therefore, it could be supposed that in the $0 < x < 1.6$ interval an isotropic increase of the unit cell volume happens, but at $x \geq 1.6$ the volume change becomes anisotropic as a result of the filling by hydrogen of those positions when the change in the c/a relation takes place [12].

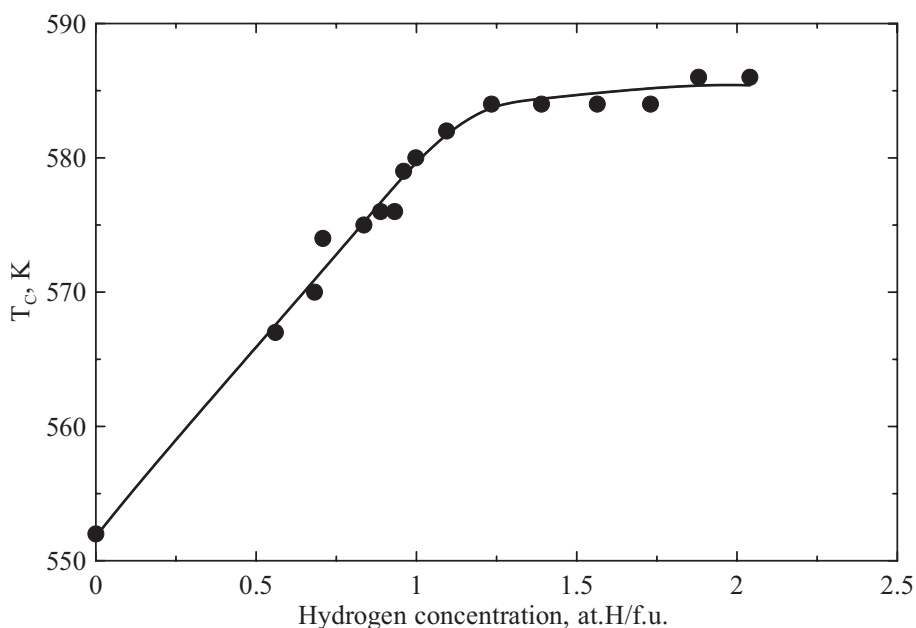


Figure 4. The dependence of Curie temperature on the hydrogen concentration for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$.

The spin-reorientation transition in $\text{Er}_2\text{Fe}_{14}\text{B}$ compound can be attributed to the competing of the uniaxial Fe sublattice and the planar rare-earth sublattice anisotropy, with the former being dominant at higher temperatures and the latter being dominant at lower ones.

Having studied the SRT temperature of $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ and K_{Fe} [13] we have calculated a B_{20} crystal field parameter before and after hydrogenation, using a formula obtained by Kuz'min et al. [14]:

$$B_{20} = \frac{20K_{\text{Fe}}}{J(J+1)(2J-1)(2J+3)} \left(\frac{k_B T_{\text{SR}}}{\Delta_{\text{ex}}} \right)^2,$$

where $\Delta_{\text{ex}} = 2 |g_J - 1| m_B B_{\text{ex}}$ – is the exchange splitting between two successive energy levels, $J = 15/2$ – quantum number of the full moment of Er^{3+} ion. Values of the exchange field B_{ex} and exchange splitting Δ_{ex} have been determined using Curie temperature data for $\text{Lu}_2\text{Fe}_{14}\text{BH}_x$ and $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ in terms of molecular field theory.

A B_{20} crystal field parameter decreases as hydrogen atoms concentration increases (Fig. 6) and, therefore, the rare-earth sublattice magnetic anisotropy constant K_{IR} ($K_{\text{IR}} \sim -J^2 B_{20} B_J^2(x)$, where $B_J^2(x)$ is the 2nd order generalized Brillouin function) also decreases. Hydrogenation leads to a decrease of the uniaxial contribution to the anisotropy K_{Fe} from the Fe sublattice [13]. Compensation of rare-earth and iron sublattices constants for the host compound takes place at temperature $T = 307$ K, and for the hydrides it takes place at higher temperature. The increase in spin-reorientation transition temperature is caused by strengthening of iron-iron and rare-earth - iron exchange interactions.

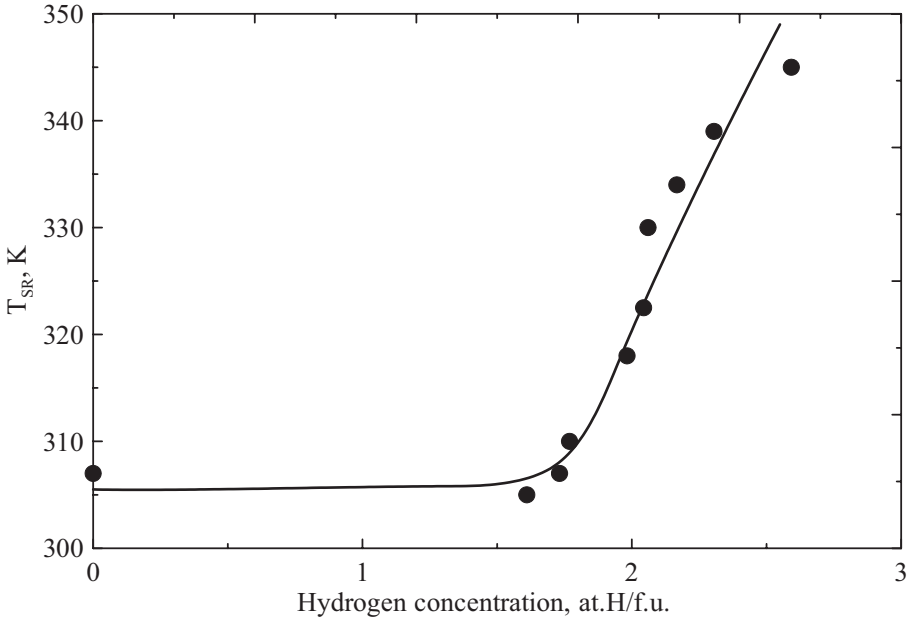


Figure 5. Temperature dependencies of magnetization and hydrogen concentration for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$ at hydrogen pressure $P = 2.5$ atm.

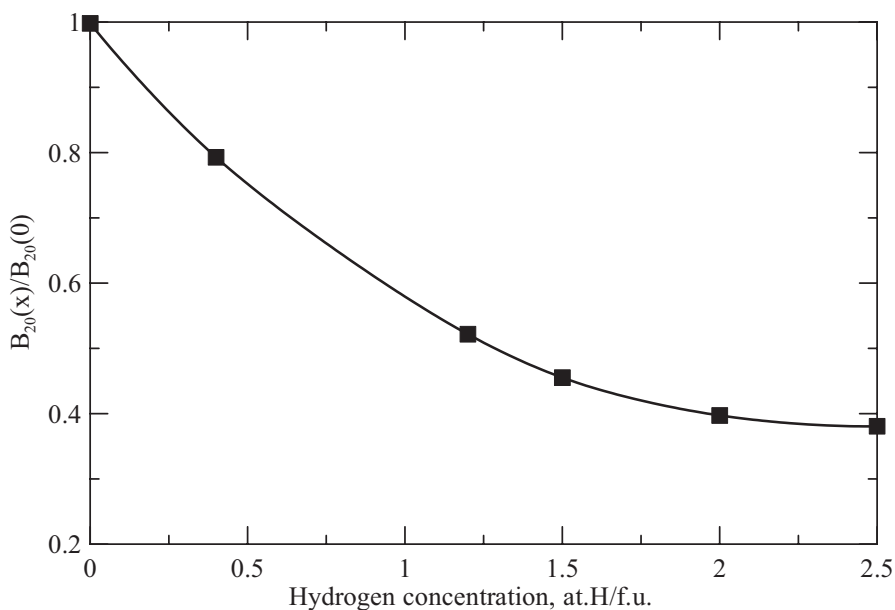


Figure 6. The dependence of the B_{20} crystal field parameter on the hydrogen concentration for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$.

4. Conclusions

We have synthesized and studied the $\text{Er}_2\text{Fe}_{14}\text{B}$ intermetallic compound and its hydrides. The dependencies of the Curie temperature and spin-reorientation temperature on the hydrogen pressure and concentration have been investigated. It has been found that T_C and T_{SR} increase monotonically as the hydrogen pressure increases. The concentration dependencies of T_C and T_{SR} on the hydrogen atoms incorporated have a different character that can be explained reasoning from the model, taking into account the dependence of exchange integrals on the unit cell volume and dependence of the magnetic anisotropy constant on the axial relation c/a . It was established that crystal fields action on the rare-earth ions considerably decreases, as the concentration of incorporated hydrogen atoms increases. The experimental results obtained are useful for understanding of the change in magnetocrystalline and exchange interactions upon the hydrogen insertion in the crystal lattice.

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THE MODERN DATA OF OBTAINING OF FIRM HYDROGEN

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Abstract. With the purpose of a solution of a problem of obtaining of firm hydrogen, the analysis of characteristics of known intensifiers and hydraulic presses for synthesis at high specific pressure of some simulated stuffs, for example of diamonds is executed. The matching of the characteristics of known rigging and equipment with idealized parameters of obtaining of metallic hydrogen has allowed to draw a conclusion that the existing means are not suitable for the solution of the given problem. The writers are offered and described the new original designs of an intensifier and presses, free from lacks known and, in case of implementation them in the metal suitable for a positive solution of the given problem.

Keywords: metallic hydrogen, intensifier, hydrostatic press, specific pressure, Mbar

1. Introduction

By problem of obtaining of firm hydrogen H the mankind began to be interested from second half XIX of century. Per second half 60 years of XX century an astrophysics of USA have opened existence on other planets H in a metallic condition and have stated a capability to synthesize metallic H in earth conditions, having reached static pressure about 3 Mbar. In activity [1] intercommunicates, that the obtaining firm H is possible at operating in an intensifier of pressure $q=2 \times 10^6$ kg/sq cm, which one twice is more q_1 , indispensable for obtaining firm argon Ar and xenon Xe.

By endorsement of veracity and capability of the practical solution of the given problem it is possible to result an example by designed Russian physicist O.Leupunsky (pronounced in due course "by an enemy of the people") theory about relation of transition of graphite in diamond from static pressure and temperature, which one informed in 1939 the journal of an academy of sciences USSR "Chemistry".

The theory guesses researches of synthesis of diamond, as in a solid phase at q up to 60 Kbar and simultaneous operating of temperature $t=2000^\circ$ C, and in a gas phase at $q=45$ Kbar and $t=1650^\circ$ C. However, for the explorers the essential concern introduced synthesis of diamond of water alone in medium of gas in chambers of the large size with the purpose of maximum growth of diamond. In this connection at the end of 60 years XX of century an item some experimenters become to create gas sources of super-high pressure (16 ... 30 Kbar), the activity with which one has appeared by extremely composite and dangerous (both explosion-dangerous, and pursued by the monopolists).

The problems of obtaining metallic H and synthetic diamond at operating super-high static pressures (in a liquid, gas and solid phase) can be successfully resolved if there is the technological tool and hydraulic presses adequate given

conditions. For example, under the data of activity [1] obtaining of bars metallic H a diameter $D=50$ mm probably on presses by an effort $P \geq 160$ thousand Tons.

Outgoing only from this condition built on Novo-Cramatorsk machine works [2,3] presses with maximum efforts $P=45...75$ thousand Tons have appeared unsuitable for the solution of the given problem. Besides on economical indexes they essentially succumbed to foreign presses of the same effort, that made scientific researches expensive, and production unprofitable.

So, for Institute of physics of high pressures Academy of Sciences of USSR was built a hydraulic press with an effort $P=50$ thousand Tons (altitude ≈ 34000 mm, weight $\approx 5,0$ thousand Tons) [2]. Was intended for synthesis of diamond of water alone by value about an egg and "«chunk" metallic H. After first and last experiment in 1978, cost 1,5 million roubles, it has appeared unsuitable for the solution of the indicated problems, about what one of the writers of the given report in 1969, 1970 years informed Academy of Sciences of USSR and Central Committee of CPSU.

The definite experience of creation of the technological tool for comprehensive loading of material is now accumulated at synthesis of diamond and other solid matters. The scheme of two versions of such tool is rotined in a Fig. 1,a and 1,b.

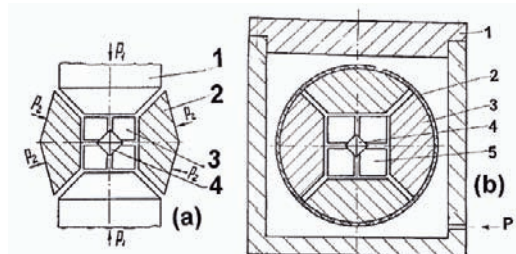


Figure 1. The schemes of comprehensive compression of solid matter 4 by hydraulic press (a), and also in a hydrostat by 1 external pressure p (b).

The scheme rotined in a Fig. 1,a is offered by V. N. Adamovich. It usage is possible on hydraulic presses transmitting an effort with the help of a slider 1 and segments 2 on solid matters by the way of an exact octagon 4 with the help eight cube 3.

In a Fig. 1,b the scheme of the device consisting of a hydrostat 1 is rotined to which one submits a liquid by pressure $p \approx 7,0$ Kbar, which one affects six spherical segments 3, protected by a rubber shell 2. The spherical segments 3 transmit efforts to solid matter 4 by the way of exact octahedron with the help of eight cube-piston 5. The sizes of spherical segments 3 pick up so, that the comprehensive pressure on solid matter 4, transmitted cube- piston 5, can reach 1,6 Mbar.

Lack introduced in a Fig. 1,a and 1,b of flow diagrams of processing of a stuff by high pressure at synthesis of diamonds is the small power stroke - from 1 up to 2 mms, and also impossibility of processing of materials in gaseousness. Similar lacks have the schemes of synthesis of stuffs, introduced in activity [4] in a Fig. 1.

2. Experimental

Allowing a large scientific and practical urgency of obtaining metallic H and considering unfitness for the solution of the given problem of the existing equipment and technological tool, the purpose of the present report was mining of perspective engineering solutions, free from lacks known.

For elimination of the given lack in Ukraine the complex of the equipment and instrumentation was built [5 ... 8]. However, on its manufacturing and intrusion under the solution CC CPSU the moratorium was overlapped, as from the party USSR there could be a competition to world corporations held by a mining of natural diamonds.

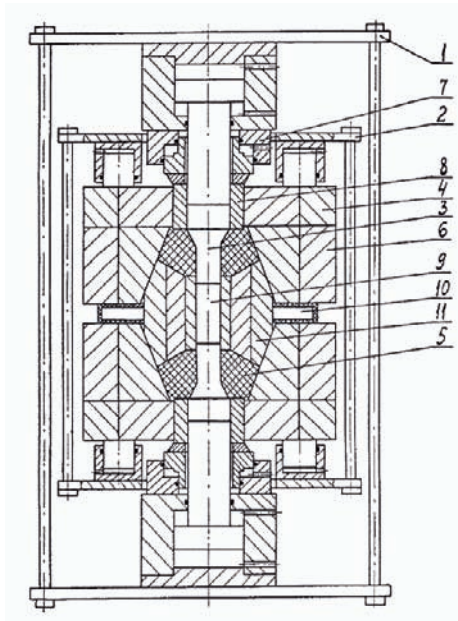


Figure 2. The scheme of an intensifier with differential support punches (DSP).

From a complex [5 ... 8] in a Fig. 2 the intensifier is rotined [8], in the scheme which one six hydraulic sources of efforts four from which one are counterbalanced by cradles 1; 2 also concentrate an effort in building bag, and the efforts of two mutually arranged sources 7, directional from center of building bag, execute differential support of an attenuators part of punches with demanded power stroke for two-eight multiple compressions, due to what it is obviously possible to treat material gaseousness. A feature of the given intensifier is that the power stroke of a plunger 3 can make 20 ... 40 mms.

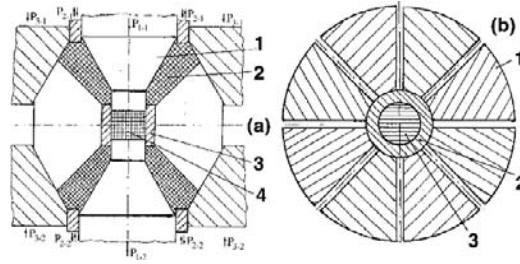


Figure 3. A unit of building bag of an intensifier with (DSP) (Fig. 2) (a), and cross-section of the same chamber (b) by a plane, perpendicular axial axes of the chamber.

In a Fig. 3,a the unit of building bag 3 (chamber conditionally is rotined in the increased kind and single-layer), in which one the material 4 is affected by a punch 1, bolstered by matter 2.

In a Fig. 3,b the cross-section of building bag 2 with actuating medium 3 by plane, perpendicular axial axes of an intensifier (Fig. 2) is rotined. The support of the chamber 2 in a tangential direction implements quadrants 1.

Small-sized press [7] by an effort up to 30 thousand T can have weight in 10...15 times smaller weights of known presses of such class. Perspective at a stage of improvement of technological methods of obtaining firm H.

Known bulkhead presses of a design Novo-Cramatorsk machine works with a maximum effort $P=45...75$ thousand T are made on machinery with the limiting characteristic, and also with usage of existing mechanics of structural materials [2, 3]. At the same time, on a known metal-working machinery with application of available structural materials, it is possible to produce offered bulky presses [6] with an effort $P \geq 160$ thousand T, which one work at external hydrostatic pressure p , created in a hydrostat or by means of immersing of a press in demanded depth of a water environment [9].

The press consists of one cylindrical tubular bench, in which one at operating pressure p two plungers move towards one to other. The working operation is committed inside a press. When the technological capabilities do not allow to produce one – frame press of demanded diameter of a working plunger [6] or cross sectional dimensions of an intensifier (Fig. 2) more minor diameter of a foramen of a bench of a press, in which one the working plunger goes, three-frame presses can be utilized (Fig. 4) [8].

The press (Fig. 4) consists of cross-pieces 1 and 16, coherent links 11 and 21. On cross-pieces three pairs of plungers 8 and 13; 4 and 15; 18 and 23 are fixed, and the diameters D_j which one content to following conditions:

$$D_4=D_{15} \text{ and } D_8=D_{13}=D_{18}=D_{23} \tag{1}$$

Plungers mutually 8 and 13; 4 and 15; 18 and 23 move towards one to other in foramens of benches 5; 9 and 20. A bench 5 - worker. However, it can miss. Instead of a bench 5 the technological tool, for example, intensifier (Fig. 2) or other tool can be built - on.

The second indispensable and sufficient working condition of three-frame presses - equality of center-to-center spacing intervals (Fig. 4):

$$XY = YZ \tag{2}$$

The idealized effort P on bar 7 (Fig. 4) is determined with the help of the following formula:

$$P = 0,25\pi p(D_4^2 + D_8^2) \quad (3)$$

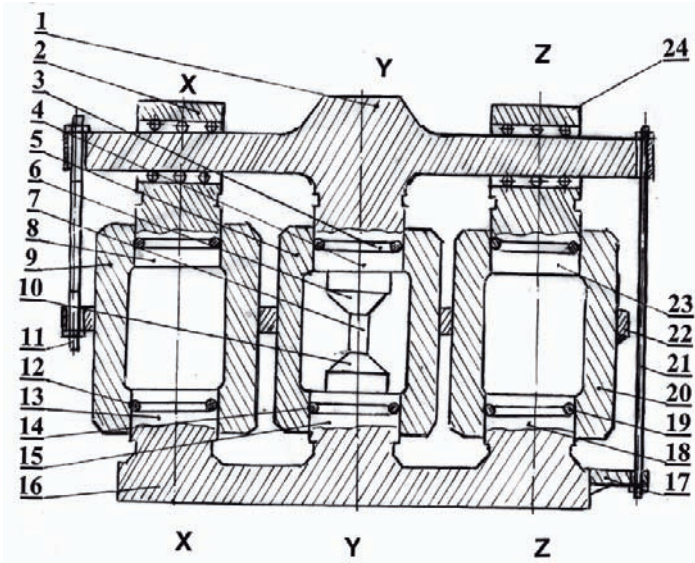


Figure 4. Three-frame hydraulic press for activity at external hydrostatic pressure p fluid mediums [6, 9].

By advantage of presses (Fig. 4 also [6]) are tight deformed condition of a bench – it corresponds to volumetric or flat compression, due to what the bench can be made from high-strength stuffs such as B_4C or SiC [10 ... 12]. The second feature - improvement of a condition of an environment, - as a pressurizing source can be utilized hydrostatic pressure of a water environment (60 % of World ocean depth of 6000 m; on this depth the hydrostatic pressure equals $p \approx 600$ kg/sq.cm).

By essential difference of offered presses (Fig. 4 also [6]) is the hermetic sealing of mobile plungers executed on the scheme barrel - seal [5]. At the expense of replacement of a sliding coupler - barrel - cylinder piston by a pair barrel - seal and selection of radial spaces under the offered mathematical formula [5], the airtightness is guaranteed, close to absolute (weight of an offset of working fluid on a surface of a rod is peer to zero point).

3. Conclusions

1. The complete set of the upgraded hydraulic presses and intensifiers of the new generation having improved technical and plant-performance figures as contrasted to known and capable to treat material under comprehensive pressure in gas medium up to 45 Kbar and solid phases up to 70 Kbar is built due to what the given equipment is perspective for the solution of a problem of creation of a master schedule of obtaining of metallic hydrogen.

2. The new design of a hydraulic press (see Fig. 4), distinguished from known hydraulic rams that works at operating external comprehensive hydrostatic pressure of a fluid medium and is perspective for creation of a master schedule of obtaining of bars of metallic hydrogen 50 ... 100 mm diameter. Such process be agrees to idealized calculations can is carried out at operating static efforts 200 ... 1000 thousand. T.

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TDS-SPECTRA OF HYDRIDE POWDER DECOMPOSITION: MODELLING WITH SIZE REDUCTION EFFECT

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Abstract. In the paper we consider the problems with moving bound that model the kinetics of hydrogen desorption from hydrides of metals. Change of phase, desorption processes and size reduction effect are taken into consideration. Equations are derived at various assumptions for the experimental method of thermal desorption spectrometry. As the high-temperature TDS-spectra peaks are considered, the diffusion may be assumed to be fast. Therefore ordinary differential equations are sufficient. We present the results of numerical experiments for the models with bulk and surface desorption.

Keywords: gas-solid reaction, metals, thermal analysis, mathematical modeling

1. Introduction

Materials suitable for hydrogen storage and transporting are being intensively searched for. Experimental research work demands development of adequate models. This helps to specify physical-chemical ideas about hydrogen interaction with solids, to discover the limiting factors and to reduce significantly the costs on experimental research by means of numerical simulation for different parameters and experimental conditions. Due to lack of space we mention only papers [1–3] which deal with this article's topic.

Nonlinear and dynamic models of desorption are used in the sequel. Mathematical justification of the boundary-value problems for the TDS-degassing method of metal saturated with hydrogen is given in [6,7]. The work [4] was a starting point of the results presented here. Algorithm of parameter identification for the model of hydrogen permeability of metals for the concentration pulses method [5] is presented in [8].

In this paper we consider only some models of TDS-dehydrogenation. A sample of powder metal hydride is placed into a chamber and relatively slowly heated under continuous evacuation. The desorption flux of hydrogen from the sample (measured by a mass spectrometer) gives information about hydrogen interaction with the studied material. Equilibrium regularities are sufficiently well studied (PTC diagrams). Growing interest is paid to kinetics of hydrogenation/dehydrogenation of metals.

We consider the material from [2] as the modelled object. Under heating ErH_3 changes as follows: $ErH_3 \rightarrow ErH_2 \rightarrow Er$ with corresponding peaks on the TDS-spectra. In this paper we consider only the high-temperature flux peak (i.e.

$ErH_2 \rightarrow Er$). Then diffusion may be considered as relatively fast and therefore ordinary differential equations are sufficient. This significantly simplifies solving the inverse problems of parameter identification. Although models with fast diffusion may also correspond to the low-temperature flux peak: atoms of H easily diffuse in ErH_2 (may be, even easier than in Er even at higher temperatures).

In the sequel material is not important, so physical and chemical terminology will be used only if necessary. A specialist decides how to interpret the word "phase" (α and β) in each specific case. For example, this may mean the pairs $ErH_2 - ErH_3$ or $Er - ErH_2$.

The effects of non-uniform heating, heat transport by diffusing particles, thermal diffusion, mechanical tensions and deformations are considered as secondary effects, i.e. comparable with the experimental errors. Heat conduction equation makes the models much more complicated. Sorption is exothermal while hydride decomposition is endothermal. We suppose that heating of the powder is almost uniform (as, for instance, in [2]). These specifications determine the range of model's adequacy. The aim of the paper is to present a few models of dehydrogenation of different complexity using minimal necessary math. These models must be simple enough so that the inverse problems of evaluation of kinetic parameters using experimental data could be solved.

2. Basic assumptions and notation

Density increases (due to volume decrease) while hydride decomposes because of lattice rearrangement. For some hydrides this effect can be significant: up to 25%. Let the sample's volume in the β phase be V , while in the α phase the same sample occupies the volume γV . Here the size reduction coefficient is denoted by γ , $\gamma < 1$. We suppose that $\gamma = \text{const}$ within the peak of TDS-spectra $T \in [T^-, T^+]$. We assume that the temperature range $T^+ - T^-$ is rather narrow. The value of γ can be easily determined.

Denote the radius of a shrinking spherical particle of powder metal hydride by $L(t)$, the radius of the shrinking hydride core by $\rho(t)$. When some amount of hydride decomposes, its volume decreases. Therefore, the decrease of the whole particle's volume can be expressed in terms of the amount of decomposed hydride: $(1 - \gamma)[\rho_0^3 - \rho^3] = L_0^3 - L^3$. Here the common factor $4\pi/3$ has been cancelled, $L_0 = L(0)$, $\rho_0 = \rho(0)$, initial time instant $t = 0$ corresponds to the beginning of the desorption peak. The mechanism of inside reduction results in tension growth. Powders of metal hydrides become finer after a few cycles of hydrogenation/dehydrogenation. We consider only fine enough powders, where tensions are not critical.

Let $c(t)$ be the concentration of corpuscular hydrogen dissolved in the outside metal skin (in α phase) with width $L - \rho$; Q be the concentration of hydrogen in hydride (β phase); $q(t)$ be the surface concentration. Traps are the defects of

metal structure, in particular, micropores. Let $z(t)$ be the concentration of hydrogen captured by traps, a_1, a_2 be the coefficients of reversible capture. The adsorption flux is μsp . Here $p = p(t)$ is the pressure of molecular hydrogen in a chamber, s is the adhesion coefficient of hydrogen to the surface, $\mu \approx 1.46 \cdot 10^{21} \text{ l/cm}^2 \cdot \text{s} \cdot \text{Torr}$ is the kinetic constant. Usually heating is linear, i.e. $T(t) = \nu t + T_0$. We assume that $c(t, r) = c(t)$ because of spherical symmetry, quick diffusion in (solid) solution, and the fact that $L \ll 1, T \gg 1$. We consider that hydrogen dissolved in hydride has left the sample by the beginning (remember that $t = 0$ corresponds to the beginning of the TDS-spectra peak). So $Q = c_\beta^{\text{crit}} = \text{const}$ is the critical concentration. During further heating β phase decomposes and desorption becomes quicker. We model the desorption flux density with a square dependence on the surface concentration (or on the concentration in the near-to-surface area): $J(t) = b(T)q^2(t)$ or $J(t) = b(T)c^2(t)$. The desorption coefficient is denoted by b in both cases, but it has different sense and different units. We assume also that all parameters depend on temperature in an Arrhenius way, in particular $b(T) = b_0 \exp\{-E_b/[RT]\}$, $b(t) = b(T(t))$. We assume that a_i are constant when $T \in [T^-, T^+]$. Dehydrating supposes that the desorption flux is more than adsorption: $\mu sp < bc^2$ or $\mu sp < bq^2$. Only some hydrogen returns back if pumping is strong. Pressure $p(t)$ and the flux density $J(t)$ are dependent: $p(t) = \theta_1 \int J(\tau) \exp\{(\tau - t)/\theta_0\} d\tau$.

This is the standard expression in metrology. If a δ -impulse of hydrogen is made in the chamber, the pressure will jump and then decrease exponentially. The constants θ_i describe the vacuum system. For a powerful vacuum system $\mu sp = 0$. The desorption flux is determined uniquely from the pressure measured by a mass-spectrometer. Formally $J = (\dot{p} + p/\theta_0)/\theta_1$ but the measurements of $p(t)$ are noisy. Therefore $J(t)$ is a solution of the integral equation of the first kind. In our article we don't consider it. We model a single particle. Taking the particle radii distribution into account we obtain rather smooth model peaks. Numerically it is sufficient to consider 10-15 values of L_0 to obtain rather smooth mean curve. The size distribution is considered to be Gaussian.

3. Models with sorption and reversible capture in the bulk

3.1. THE SIMPLEST MODEL

Suppose that hydride decomposition is fast enough to maintain the equilibrium concentration in the solution $c(t) = \bar{c}$. Desorption outflow is compensated by hydride decomposition. Desorption is bulk. This means that the material is sufficiently porous, so $J = bc^2$. In general case $Q = Q(T)$, $\bar{c} = \bar{c}(T)$. We can suppose that Q and $\bar{c}$ are constant within the thin peak of TDS-spectra for the

material. Left and right walls of PTC-diagrams are almost vertical at $T \in [T^-, T^+]$. So $c(t) \equiv \bar{c}$ ($\bar{c} < Q$), $L(t)$ decrease while $\rho(t) > 0$. This means that the concentration doesn't change while there is some hydride left. Hydride vanishes at $t = t_*$: $\rho(t_*) = 0$. After that $\rho(t) = 0$, $L(t) = L(t_*)$, and $c(t)$ decreases monotonically. Let us consider these two stages. We suppose that the defects are small:

$$\dot{z} = a_1 c - a_2 z, \dot{z} = 0, t < t_* \Rightarrow z = \bar{z}, a_2 \bar{z} = a_1 \bar{c}, \bar{c} + \bar{z} < Q.$$

The balance equation for decomposing hydride is:

$$QV(L_0) = QV(\rho(t)) + (\bar{c} + \bar{z})(V(L(t)) - V(\rho(t))) + \int_0^t \{b(\tau)\bar{c}^2 - \mu s(\tau)p(\tau)\}S(L(\tau))d\tau.$$

Here $V(r)$ is for volume of a sphere, $S(r)$ is for its surface. Differentiating on t :

$$\{\mu s p - b\bar{c}^2\}L^2 = [Q - \gamma(\bar{c} + \bar{z})]\rho^2 \dot{\rho}, \quad (1 - \gamma)\rho^2 \dot{\rho} = L^2 \dot{L},$$

$$L(t) = \frac{1 - \gamma}{Q - \gamma(\bar{c} + \bar{z})} \int_0^t \{\mu s p - b\bar{c}^2\} d\tau + L_0. \quad (1)$$

The hydride core radius $\rho(t)$ is determined by $L(t)$: $(1 - \gamma)[L_0^3 - \rho^3] = L_0^3 - L^3$.

From this expression one can numerically obtain the time t_* when hydride vanishes, i.e. $\rho(t_*) = 0$.

Now let us consider hydrogen balance on the second stage ($t > t_*, \rho \equiv 0, L = L_* = L(t_*)$):

$$[c(t + \Delta t) - c(t)]V(L_*) + [z(t + \Delta t) - z(t)]V(L_*) = \{\mu s(t)p(t) - b(t)c^2(t)\}S(L_*)\Delta t + o(\Delta t).$$

Dividing this on $\Delta t \rightarrow 0$ we obtain the system: $c(t_*) = \bar{c}$, $z(t_*) = \bar{z}$,

$$\dot{c} = 3L^{-1}\{\mu s p - b\bar{c}^2\} - a_1 c + a_2 z, \quad \dot{z} = a_1 c - a_2 z, \quad a_1 \bar{c} = a_2 \bar{z}. \quad (2)$$

Note that in the simplest model $\dot{\rho} \rightarrow -\infty$ as $t \rightarrow t_*$. But velocity of the phase interface is obviously bounded. Decomposing hydride at $\rho \rightarrow 0$ is not able to maintain the equilibrium concentration uniformly with respect to the radius of the particle. This disadvantage of the model is not too bad. Volume of the core decreases as ρ^3 . We can numerically switch to degassing stage when $\rho < L/10$.

This switch doesn't influence on diagram of J . The advantages are the low number of parameters (they can be estimated using a little experimental data). Model curves satisfactorily approximate the experimental data if distribution is taken into account. Also we bear in mind that the algorithms of parameter identification are locally convergent. The parameter estimations of simple models should be taken as the initial approximation for more complex models.

3.2. A SWITCHING MODEL

In the beginning ($\rho_0 = L_0$) potential hydride decomposition flux exceeds desorption flux: $I = k(T)Q > b(T)\bar{c}^2$. Hydride decomposes with the rate necessary to maintain the equilibrium $\bar{c}$ in α phase. When at $\rho \rightarrow 0$ this will be impossible,

$c(t)$ begins to decrease. The switch condition follows from the equality of the fluxes:

$$k(t_s)Q\rho^2(t_s) = \{b(t_s)\bar{c}^2 - \mu s(t_s)p(t_s)\}L^2(t_s). \quad (3)$$

Consider the time segment $[0, t_s]$. Then $c(t) \equiv \bar{c}$. The radius L satisfies (1).

Substituting $L(t)$ and $\rho(t)$ in (3), we get an equation for t_s . It can be effectively numerically solved by Newton's method. Now consider $t \geq t_s$. Hydride decomposes with the highest possible rate. Rate of the concentration decrease is determined by the difference of the desorption flux and the flux from the hydride. The total balance for $t > t_s$ is:

$$QV(\rho) + [c(t) + z(t)][V(L) - V(\rho)] + \int_{t_s}^t \{bc^2 - \mu sp\}S(L(\tau))d\tau = \text{const.}$$

Differentiating on t , we get

$$\{\mu sp - bc^2\}L^2 = [Q - \gamma(c + z)]\rho^2\dot{\rho} + [\dot{c} + \dot{z}][L^3 - \rho^3]/3. \quad (4)$$

Now consider the balance near the phase bound:

$$-[Q - \gamma(c(t) + z(t))]\Delta V = I(t)S(\rho(t))\Delta t + o(\Delta t) \quad (\Delta V < 0).$$

From here we get the Stefan condition. This is the equation for $\rho(t)$, $\dot{\rho} < 0$:

$$[Q - \gamma(c(t) + z(t))]\dot{\rho}(t) = -I(t), \quad I(t) = k(t)Q, \quad \rho(t_s) = \rho_s. \quad (5)$$

Initial data ρ_s are defined by the stage $t < t_s$. Substituting (5) in (4), we get the equation for the concentration $c(t)$. Here are the model equations in the compact form:

$$\begin{aligned} 0 < t < t_s : \quad c &\equiv \bar{c}, \quad L(t) = \frac{1-\gamma}{Q-\gamma(\bar{c}+\bar{z})} \int_0^t \{\mu sp - b\bar{c}^2\}d\tau + L_0, \\ (1-\gamma)(\rho^3 - \rho_0^3) &= L^3 - L_0^3, \quad \rho_0 = L_0, \quad a_2\bar{z} = a_1\bar{c}, \\ t > t_s : \quad (L^3 - \rho^3)\dot{c} &= 3[I\rho^2 + (\mu sp - bc^2)L^2] - \dot{z}(L^3 - \rho^3), \\ (Q - \gamma(c + z))\dot{\rho} &= -I, \quad I = kQ, \quad \dot{z} = a_1c(t) - a_2z(t), \quad z(t_s) = \bar{z}, \quad c(t_s) = \bar{c}. \end{aligned}$$

The concentrations $c(t)$ and $z(t)$ begin changing smoothly: $\dot{c} = \dot{z} = 0$, $t = t_s$, $\dot{\rho}(t_s + 0) = \dot{\rho}(t_s - 0)$. Degassing stage at $t \geq t_s$ is described by equations (2). Only the initial data are different: in $\dot{c} = \dots$ we must switch to $\rho \equiv 0$, $L = L_* = L(t_s)$, $t \geq t_s$.

3.3. SELF-CONTROL OF HYDRIDE DECOMPOSITION VELOCITY

We suppose here that the flux balance from the very beginning determines the dynamics of the dissolved hydrogen concentration. Flux balance is determined by the difference of the desorption flux and the flux from the hydride phase. Desorption is bulk. To avoid singularity in the obtained differential equations at $t = 0$ we should consider an "initial skin": a thin layer of metal with dissolved hydrogen around the hydride core. Initial cover appears at the preliminary stage of the TDS experiment before the TDS-splash begins. We model the density of the

hydrogen atom flux from the hydride phase as $I(t; T, Q, c, \bar{c}) = k(t)Q[1 - c/\bar{c}]$. The factor in brackets describes how the concentration of dissolved hydrogen influences on the flux from the hydride phase: the lower the concentration, the greater the flux. If the concentration $c(t)$ is near to equilibrium, the flux will be significantly lower than the highest possible. Hydrogen desorption outflow doesn't allow $c(t)$ to exceed the level $\bar{c}$ since from $c = \bar{c}$ it follows that $I = 0$. From the balance equations we derive the equations for $c(t)$ and $\rho(t)$ in the same way as 3.1. These equations are not changed significantly. We only replace $I = kQ$ with $I = kQ[1 - c/\bar{c}]$ and choose $\rho_0 < L_0$ so that $L_0 - \rho_0 \ll 1$. Diffusing hydrogen in hydride and slow initial decomposition of β phase form the initial skin of α phase. These processes are initiated by the bulk desorption. Then equal concentrations $c(t) = c_0 < \bar{c}$ and $z_0 = c_0 a_1 / a_2$ are maintained. Bulk desorption has much time to reduce hydrogen concentration in near-to-surface area and create initial cover of α phase while doesn't begin intensive decomposition of β phase under further heating. These processes are continued up to $c_\beta = Q$. Almost all hydrogen is located in β phase. The moderate variation of initial data don't influence on J .

4. Models with surface

4.1. THERE ARE DIFFERENT ARGUMENTS OF CONSIDERING THE SURFACE

Among them are the presence of dirt and oxidation films which can significantly change properties of material. Let $q(t)$ be the surface concentration. We assume that a condition of quick solution take place in the range of TDS peak: $c(t) = g(t)q(t)$, $g(t) = g(T(t)) \approx \text{const}$. It can be obtained from the condition that the difference of the solution into the bulk and the return to the surface fluxes is taken away by diffusion: $D(T)c_r(t, L) = k^-(T)q(t) - k^+(T)c(t, L)$, provided that both terms at the right part are significantly greater than the left part and the activation energies of k^+ , k^- are almost equal, i.e. the surface is isotropic. Then $g = k^- / k^+ = \text{const}$, $T \in [T^-, T^+]$. The balance is

$$QV(\rho) + [c(t) + z(t)][V(L) - V(\rho)] + q(t)S(L) + \int_0^t \{bq^2 - \mu sp\} S(L(\tau)) d\tau = QV(L_0).$$

Differentiating on t and considering $L^2 \dot{L} = (1 - \gamma)\rho^2 \dot{\rho}$ we get

$$[Q - \gamma(c + z)]\rho^2 \dot{\rho} + [\dot{c} + \dot{z}](L^3 - \rho^3)/3 + \dot{q}L^2 + 2L\dot{L}q + \{bq^2 - \mu sp\}L^2 = 0.$$

In order to get an equation for $q(t)$ we must substitute $c = gq$, $\dot{\rho} = -I/[Q - \gamma(c + z)]$ and $\dot{z} = a_1 c - a_2 z$. Initial data are $q_0 = c_0 / g$, $\rho_0 = L_0$, $c_0 \leq \bar{c}$, $a_2 z_0 = a_1 c_0$.

4.2. HERE WE CONSIDER A MORE COMPLEX SOLUTION CONDITION

Dynamics of $q(t)$ is

$$\dot{q}(t) = \mu s(t)p(t) - b(t)q^2(t) + I_s(t), \quad q_0 \leq \bar{q} = q_{\max}.$$

Here $I_s(t)$ is for the density of the flux from the bulk to the surface, $I_h(t)$ is for the density of the flux from the hydride phase. Differentiating the balance we get:

$$[\dot{c}(t) + \dot{z}(t)] \frac{L^3(t) - \rho^3(t)}{3L^2} - I_h(t) \frac{\rho^2}{L^2} + 2q \frac{\dot{L}}{L} + I_s(t) = 0.$$

The Stefan condition $I = I_h$ and the equation for $z(t)$ remain the same. Flux densities can be modelled by $I_h(t) = k_h(t)Q[1 - c(t)/\bar{c}]$, $I_s(t) = k_s(t)c(t)[1 - q(t)/\bar{q}]$. Values of $c_0 \approx \bar{c}$, $q_0 \approx \bar{q}$ and the velocities $\dot{\rho}(0)$, $\dot{c}(0)$ are not too large.

5. A Model with relatively fast diffusion

In this section we cancel the supposition that diffusion is too fast and thus $c(t, r) = c(t)$. Instead we suppose that diffusion in the solution is quick enough compared to the processes on the phase bound and on the surface, but not quick enough to make $c(t, r)$ constant with respect to r . Let the function $c(t, r)$ satisfy the diffusion equation

$$c_t = D(t)[c_{rr} + 2c_r/r], \quad \rho(t) < r < L(t), \quad D(t) = D_0 \exp\{-E_D/[RT]\}, \quad T = T(t).$$

Suppose processes on the bounds $r = \rho(t)$, $L(t)$ are relatively slow compared to the diffusivity D and thus the concentration profile changes slowly; then we can consider the equation $c_{rr} + 2c_r/r \approx 0$. Integrating this second-order equation we get the "quasi-stationary" concentration profile $c(t, r) = A(t) + B(t)/r$, $r \in [\rho(t), L(t)]$, $\rho_0 < L_0$, $(1 - \gamma)(\rho^3 - \rho_0^3) = L^3 - L_0^3$. Thus concentration as a function of r is always stationary (a hyperbola). Parameters A and B are determined by the flux balance from the hydride phase and desorption. The concentration $c(t, r)$ obviously decreases with respect to $r \in [\rho, L]$ if we consider dehydrogenation. Therefore $B(t) > 0$. As the fluxes change and the core gradually shrinks, the stationary distribution changes, but slowly compared to diffusion. The sense of the prefix "quasi" is that $A = A(t)$, $B = B(t)$ and $\dot{A} \approx 0$, $\dot{B} \approx 0$ relatively.

Let desorption be bulk and the defects be small. The balance is

$$QV(\rho) + 4\pi \int_{\rho(t)}^{L(t)} r^2 c(t, r) dr + 4\pi \int_0^t \{b(\tau)c^2(\tau, L(\tau)) - \mu s(\tau)p(\tau)\} L^2(\tau) d\tau = \text{const.} \quad (6)$$

Differentiating on t and considering $[Q - \gamma c(t, \rho)]\dot{\rho} = -I$, $c(t, r) = A + B/r$ we get

$$I\rho^2 \frac{Q - A - B\rho^{-1}}{Q - \gamma(A + B\rho^{-1})} - L^2 \dot{L}c(t, L) + [\mu sp - bc^2(t, L)]L^2 = \dot{A} \frac{L^3 - \rho^3}{3} + \dot{B} \frac{L^2 - \rho^2}{2}. \quad (7)$$

To determine the functions $A(t)$ and $B(t)$ we need one more equation. Diffusion inflow to the surface is taken away by desorption:

$$bc^2(t, L) = -Dc_r(t, L) \Rightarrow b[A + B/L]^2 = DBL^{-2}. \quad (8)$$

This expression allows to exclude A from (7) and the Stefan condition. As a result we obtain the system of differential equations $\dot{\rho} = f_1(\rho, B)$, $\dot{B} = f_2(\rho, B)$, $\rho_0 < L_0$.

We need to specify the value of $B_0 = B(0)$. There are a few possibilities. In case of local equilibrium initial concentration $c(0, \rho_0) = \bar{c}$ (in view of (8) $A = A(B)$):

$$A + B/\rho_0 = \bar{c}, (\sqrt{BD/b} - B)/L_0 + B/\rho_0 = \bar{c}, t = 0.$$

The last equation is a square equation with respect to $\sqrt{B_0}$. The roots of this equation have a different signs. We choose the positive root. Using this root we find B_0 and the distribution $c(0, r) = A_0 + B_0/r$, $r \in [\rho_0, L_0]$. Instead of $c(0, \rho_0) = \bar{c}$ we can assume that $I(0) = -Dc_r(0, \rho_0) = D(0)B(0)\rho_0^{-2}$, i.e. hydride decomposition at initial point of TDS-spectra corresponds to diffusion on the phase bound and the "smooth start" take place. Choosing $\rho_0 < L_0$, $\rho_0 \approx L_0$ influences weakly on the J since concentration of hydrogen atoms in thin layer of solution is essentially smaller than that in the hydride core.

We model hydride decomposition as $I(t) = k(t)Q$, $I(t) = k(t)Q[1 - c(t, \rho)/\bar{c}]$, $k(t) = k(T(t))$. In last case we should choose $c(0, L) = c_0 < \bar{c}$. Hyperbola transforms to a line $c(t) = A(t)$ at the moment t_* when hydride vanishes ($\rho(t_*) = 0$). Degassing stage is described by $L_*\dot{c}(t) = 3[\mu sp - bc^2(t)]$.

6. Distributed models

In conclusion we consider the models for TDS-spectra of dehydrogenating when diffusion is significant. We assume that all parameters depend on temperature in an Arrhenius way. Due to paper's size limitations we are not able to discuss how to construct difference schemes. They have been developed for the nonlinear distributed models with moving bounds. Here $c = c(t, r)$, the other notation is the same.

6.1. MODEL WITH BULK DESORPTION

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \left[D \frac{\partial c}{\partial r} - c(t, r)v(t, r) \right] \right), \quad t \in (0, t_*), \quad r \in (\rho(t), L(t)), \quad (9)$$

$$(\underline{Q} - \gamma c(t, \rho)) \dot{\rho}(t) = D(t) \frac{\partial c}{\partial r} \Big|_{\rho(t)}, \quad \rho(0) = \rho_0 < L_0, \quad (10)$$

$$I_\rho \equiv k(t) \underline{Q} [1 - c(t, \rho) / \bar{c}] = -D(t) \frac{\partial c}{\partial r} \Big|_{\rho(t)}, \quad (11)$$

$$D(t) \frac{\partial c}{\partial r} \Big|_L = -b(t) c^2(t, L), \quad L(t) = L(\rho(t)), \quad (12)$$

$$c(0, r) = A + B/r: \quad c(0, \rho_0) = c_h < \bar{c}, \quad c(0, L_0) = c_0 < c_h, \quad r \in (\rho_0, L_0). \quad (13)$$

Here $v(t, r) = (1 - \gamma) \rho^2 \dot{\rho} r^{-2}$ is the velocity of moving along radius of metal layer ($\dot{V}(r) = \dot{V}(L)$). If potential hydride decomposition velocity is significantly higher than the diffusion velocity then we have local equilibrium $c(t, \rho(t)) = \bar{c}$ instead of equation (11). Singularity at $r \rightarrow 0$ is not dangerous. Taking into account the spherical symmetry we have $c_r \rightarrow 0$ and $c_t \approx 3Dc_{rr}$ at $r \approx 0$. The volume of core decreases as ρ^3 . We can numerically switch to degassing stage when $\rho < L/10$. We don't consider this stage here.

6.2. MODEL WITH SURFACE DESORPTION: to (9)–(11) we add $c(0, r) = \bar{c}$ and

$$-D(t) \frac{\partial c}{\partial r} \Big|_L = k^+(t) c(t, L) (1 - \theta^-) - k^-(t) q(t) (1 - \theta^+), \quad (14)$$

$$\theta^- = q / \bar{q}, \quad \theta^+ = c(t, L) / \bar{c}, \quad \bar{c} = g \bar{q}, \quad g = k^- / k^+, \quad (15)$$

$$\dot{q}(t) = \mu s(t) p(t) - b(t) q^2(t) - 2q(t) \dot{L}(t) L^{-1}(t) - D(t) \frac{\partial c}{\partial r} \Big|_L, \quad q(0) = \bar{q}. \quad (16)$$

We also can use hyperbolic distribution $c(0, r) = \varphi(r)$. If diffusion and desorption are limiting then we have $c(t, \rho) = \bar{c}$, $c(t, L) = g q(t)$ instead of (11), (14), (15). This reduces the number of unknown a priori parameters and simplifies the numerical solution.

7. The results of numerical experiments

We assume that the evacuating system is powerful enough and therefore very small amount of desorbed hydrogen returns back to the surface, i.e. $\mu_{sp} \approx 0$. Together with the desorption flux density curves here are the scaled concentration curves and radius of moving phase bound curves. Heating is linear. The pictures illustrate the impact of different kinetic parameters. Parameters' values correspond to the curves in the following way: the first value is for the curve with the highest maximum, the last is for that with the lowest maximum. The dagger shows the switch time, i.e. the time when the decomposition flux and the desorption flux became equal. The tiny circle shows the time of hydride disappearance. We take into consideration size particle distribution by smoothing the curves using 15 radii during numerical modelling. This amount was enough to make the resulting curve smooth.

On Fig. 1 one can see a desorption flux density J together with the scaled curves of the concentration $c \cdot \max J / [1.5 \max c]$, hydride core radius $\rho \cdot \max J / [2 \max \rho]$ and the particle radius $L \cdot \max J / [1.7 \max L]$ for the simplest model (3.1). Parameters are as follows: $b_0 = 1.7 \cdot 10^{-20} \text{ cm}^4/\text{s}$, $E_b = 112 \text{ KJ/mole}$, $\bar{c} = \eta Q$, $\eta = 0.15$, $Q = 1.5 \cdot 10^{22} \text{ cm}^{-3}$, $\dot{T} = 0.3 \text{ K/s}$, $T(0) = 670 \text{ K}$, $L_0 = 5 \cdot 10^{-3} \text{ cm}$, $a_1 = 0.2 \text{ s}^{-1}$, $a_2 = 0.1 \text{ s}^{-1}$, $\gamma = 3/4$. For Fig. 2 the parameters are the same except $a_1 = 0.1$. The curves differ from each other: 1) $L_0 = 8 \cdot 10^{-3}$ (the highest maximum); 2) with distribution of particle radii (mean radius is $\bar{L}_0 = 5 \cdot 10^{-3}$, $L_0^{\min} = 2 \cdot 10^{-3}$, $L_0^{\max} = 8 \cdot 10^{-3}$); 3) smoothed by traps ($a_1 = 0.5$); 4) $L_0 = 2 \cdot 10^{-3}$ (the lowest maximum).

Figure 3 illustrates the switch model (3.2). Parameters are $b_0 = 6 \cdot 10^{-20}$, $E_b = 121$, $\bar{c} = \eta Q$, $\eta = 0.15$, $Q = 1.5 \cdot 10^{22}$, $\dot{T} = 0.3$, $T(0) = 670$, $L = 0.005$, $k_0 = 1.2 \cdot 10^{-5}$, $E_k = 0$, $a_1 = 0.15$, $a_2 = 0.2$, $\gamma = 0.9$. For Fig. 4 the following parameters of Fig. 3 are changed: ($k_0 = 10^{-5}$, $a_2 = 0.1$, $\gamma = 0.75$): $b_0 = 6 \cdot 10^{-20}$, $E_b = 110$, $a_1 = 0.25$; $b_0 = 6 \cdot 10^{-20}$, $E_b = 120$, $a_1 = 0.35$; $b_0 = 2 \cdot 10^{-21}$, $E_b = 120$, $a_1 = 0.35$. On Fig. 5 one can see the traps impact for model 3.2. Basic parameters are the same (Fig. 3), changes are: $a_1 = 0.1$, $a_2 = 0.5$; $a_1 = 0.4$, $a_2 = 0.4$; $a_1 = 0.5$, $a_2 = 0.1$. If absorption factor doesn't exceed isolation factor then plot is sharp, otherwise it is smooth.

The parameters of Fig. 6 for the model with self-control of hydride decomposition (3.3.): $b_0 = 6 \cdot 10^{-18}$, $E_b = 157$, $\bar{c} = \eta Q$, $\eta = 0.15$, $Q = 1.7 \cdot 10^{22}$, $\dot{T} = 0.3$, $T(0) = 670$, $L = 0.005$, $k_0 = 5 \cdot 10^{-5}$, $a_1 = 0.1$, $a_2 = 0.1$, $\gamma = 3/4$. Changes are: $E_k = 5; 10; 15$.

Figure 7 illustrates the influence of heating rate for the model with surface. Parameters are $b_0 = 10^{-9}$, $E_b = 202$, $\bar{c} = \eta Q$, $\eta = 0.15$, $g = 22500$, $Q = 7.0477 \cdot 10^{23}$, $T(0) = 670$, $L = 7.5 \cdot 10^{-5}$, $k_0 = 0.15$, $E_k = 100$, $a_1 = 0.1$, $a_2 = 0.1$, $\gamma = 3/4$.

On Fig. 8 we compare the experimental flux density curve $J_m(T)$ with those obtained from model 3.3: $I(t) = k(t)Q[1 - c/\bar{c}]$. Basic parameters are the same (Fig. 6). Changes are $b_0 = 7 \cdot 10^{-18}$, $E_b = 153$, $Q = 1.65 \cdot 10^{22}$, $E_k = 4$, $a_2 = 0.15$, $\gamma = 0.88$. Approximations of the same experimental data are shown for the switch model and the size reduction effect. Parameters are the same as for Fig. 3. The plots move right. One can see that it is difficult to choose a model. Experimental errors can be up to 20%. Therefore a single experiment with linear heating doesn't provide enough information. A series of experiments with different heating rates and even different heating laws is necessary to specify the dehydrating mechanism. Changing $\nu = \dot{T}$ shows that even different heating rates can fail to distinguish the models. Thus more complicated cases should be considered. For distinctness we

choose the model 3.3. It is relatively easy to realize a “sawtooth” heating law of heating/cooling (Fig. 9). Period is 500s, $T(0) = T_{\min} = 670\text{K}$, $T_{\max} = 938\text{K}$. Heating and cooling rates are equal. One can see a desorption flux density $J(t)$ together with $c \cdot \max J / [1.5 \max c]$, $\rho \cdot \max J / [2 \max \rho]$ and $L \cdot \max J / [2 \max L]$. Parameters are the same as for Fig. 6.

On Fig. 10 there are a plot of the flux density $J(T)$, scaled curves $A \cdot \max J / [1.2 \max A]$, $B \cdot \max J / [2 \max B]$ for a model with relatively fast diffusion. Parameters are $b_0 = 3 \cdot 10^{-20}$, $E_b = 120$, $D_0 = 8 \cdot 10^{-4}$, $E_D = 50$, $\bar{c} = \eta Q$, $\eta = 0.15$, $Q = 1.5535 \cdot 10^{22}$, $T(0) = 670$, $\dot{T} = 0.3$, $L = 5 \cdot 10^{-3}$, $\rho_0 / L = 0.96$, $k_0 = 5 \cdot 10^{-5}$, $E_k = 25$, $\gamma = 3/4$.

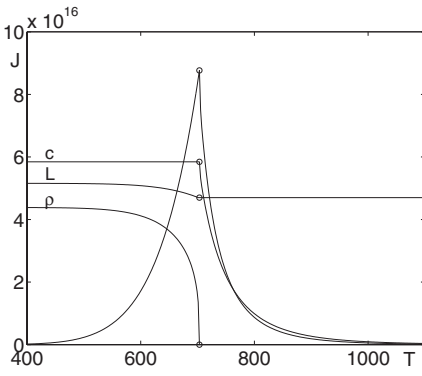


Figure 1. Model 3.1, one particle.

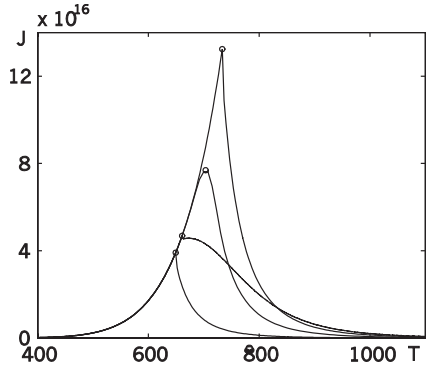


Figure 2. Model 3.1, powder.

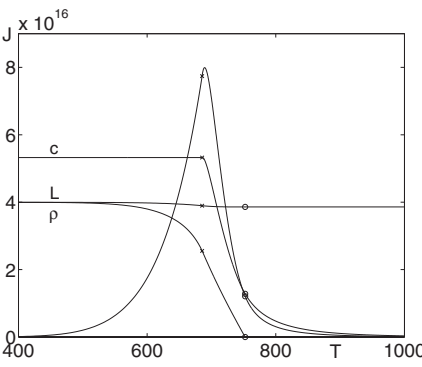


Figure 3. Model 3.2, one particle.

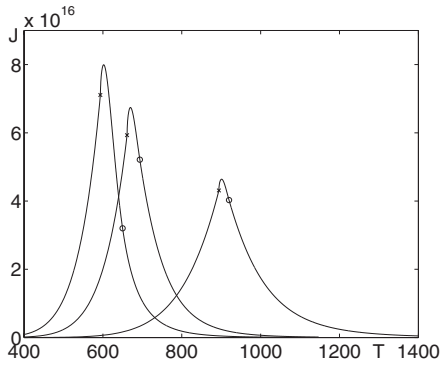


Figure 4. Model 3.2, the impact of E_b and b_0 .

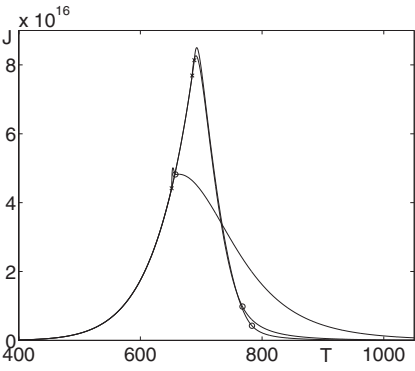


Figure 5. Model 3.2, the impact of traps.

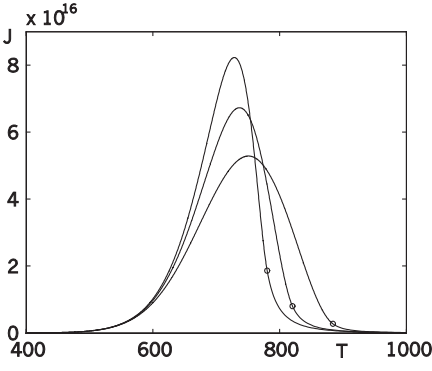


Figure 6. Model 3.3, the impact of parameter E_k .

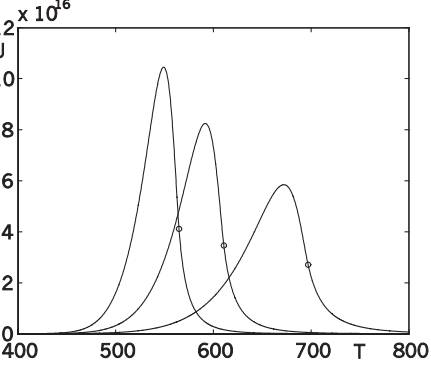


Figure 7. Model 4.1, $\dot{T} = 0.4; 0.3; 0.2$.

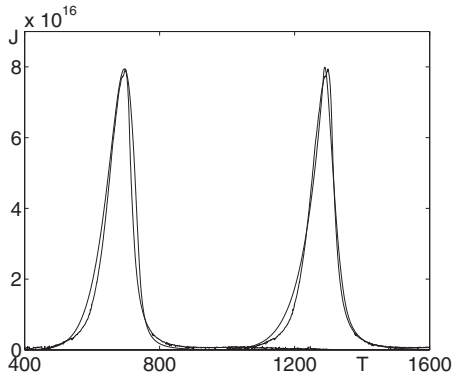


Figure 8. Model 3.3, approximation of J_{ex} .

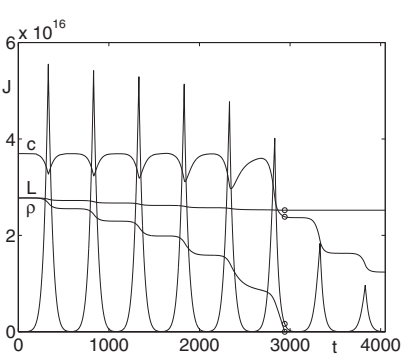


Figure 9. Model 3.3, "sawtooth" heating.

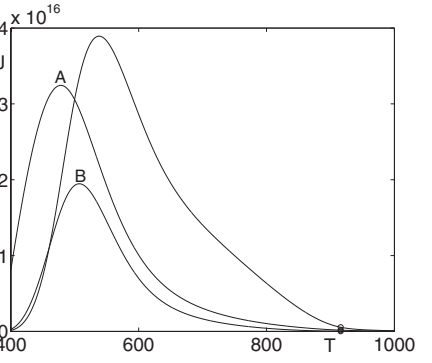


Figure 10. Model 5, J, A, B .

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ACTIVATED CARBON AND HYDROGEN ADSORPTION STORAGE

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Abstract. Activated carbons were chosen as an efficient hydrogen sorption materials to design gas storage systems. Based on experimental data empirical dependences for choosing commercially available carbon hydrogen sorbents systems were proposed. To increase gas sorption capacity technology of carbon additional activation was applied.

Different heat pipe devices for sorbent bed thermal control were developed for integrating in sorption storage vessels. Developed theoretical model of cylindrical AG vessel with internal finned heater (HP based) can be used for storage systems designing.

The designed AGS systems and modified carbon sorbents are perspective for the hydrogen storage and for two-fuel automobile

Keywords: Carbon, hydrogen, sorption, heat pipe, adsorption storage

1. Introduction

From environmental point of view hydrogen is the cleanest known fuel, and from economic point of view hydrogen technology will be able to revolutionize the transport and energy market. Now hydrogen becomes the real alternative for fossil fuel systems. Among the advantages of hydrogen are its low density and small volume heat of combustion. But recently none of the existing methods of hydrogen storage is efficient in terms of energy density, of neither a volume nor mass and gas release rate. From the application point of view it is vital to find the most effective way to store hydrogen and then, to replace the current fuel systems.

Hydrogen storage by solid materials is the most recent system proposed [1]. Initially the research was based on cryogenic systems [2], now the studies have focused in the search of the high capacity adsorbent to be used at room temperature. Due to the high density of the adsorbed phase (it corresponds to density of pressurized gas at 60 – 80 MPa) the gas storage capacity in the vessel with sorbent can increase significantly. Since it is close to the liquid density, the volumetric capacity of adsorption system is predicted to be higher then for compression system. Activated carbons, activated carbon fibers and graphite nanofibers are perspective candidates for hydrogen adsorption storage. Many metals, alloys and intermetallic compounds can also reversible adsorb large amounts of hydrogen. However, none of them is known practically effective for the mobile storage applications.

The objective of this work is to analyze hydrogen storage in several porous carbon-based materials with different porous structures to propose perspective activated carbons (carbon fibers) for high performance hydrogen storage systems, to suggest methods of its hydrogen adsorption properties improvement. Another interrelated work objective is development of thermally regulated adsorption storage system for dual-fuel (hydrogen and natural gas) automobile. In fact, such gases as methane, ammonia, methanol, etc can be considered as hydrogen storages by itself also.

2. Carbon materials as a storage medium for gases

Activated carbon is well known as one of the best adsorbents for gases [3]. In contrast to the chemisorption in metal hydrides [4], the phenomenon of physical adsorption is essentially accumulation of the undissociated hydrogen molecules on a surface of microporous carbon fibers or particles. This property is due to ability of carbon to be prepared in a very fine powdered or fiber form with highly porous structure and due to specific interactions between carbon atoms and gas molecules. The total amount of adsorbed hydrogen strongly depends on the pore geometry and pore size distribution as well as the storage pressure and temperature. Recently many improvements have been accomplished to obtain microporous carbonaceous materials with extremely high adsorbing properties for different gases [5]. Adsorption of methane and hydrogen are usually takes place in micropores. Macropores have no practically influence on the adsorption capacity, as they are only important for the gas compression and for adsorption/desorption reaction rates [6]. Due to its high surface area and abundant pore volume, activated carbon is considered as good adsorbent. For conventional activated carbon, the hydrogen uptake is proportional to its surface area and pore volume, while, unfortunately, a high hydrogen adsorption capacity (4 ~ 6 wt%) can be only obtained at very low cryogenic temperatures or very high pressures. To gain the goal of the problem – efficient methane and hydrogen storage and transportation it is necessary to develop a high performance microporous adsorbent material and an advanced system of the vessel thermal control.

Thus, the cheap activated carbon fabricated by special thermal treatment of impregnated raw (wood, sawdust, cellulose, straw, paper for recycling, peat etc.) is attractive for modern sorption technologies. The use of specific organic and non-organic compounds as raw impregnates offers production activated carbons with controlled porous structure and high yield (up to 50 wt %). Developed advanced technology allows to produce the homogeneous carbon adsorbents with benzene pore volume 0,3 – 0,6 cm³/g (70 – 80 % - volume of micropores), nitrogen surface area up to 1500 m²/g, iodine adsorption capacity 40 – 70 wt % and methane adsorption capacity up to 160 mg/g (3.5 MPa, 293 K). Impregnated cellulose - containing raw for manufacture special activated carbon materials for ammonia, methane and hydrogen storage systems with high microporosity, surface area and narrow micropore size distribution is the attractive host material for adsorption of different gases. The activated carbon fiber “Busofit” and activated wood-based carbon particles ([7], the Institute of General and Inorganic Chemistry, NASB) fabricated in Belarus are perspective materials for gas storage systems (Figs. 1 – 2).

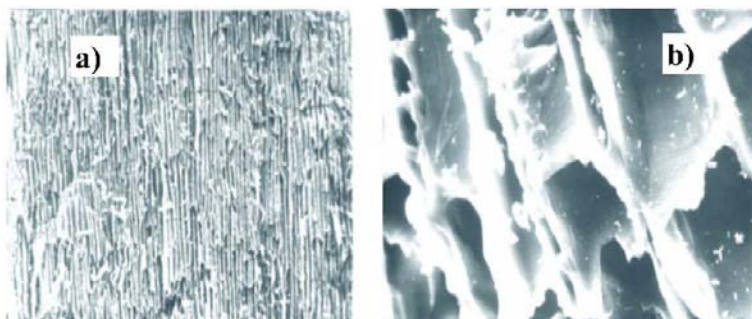


Figure 1. Active carbon material made from waste wood (IGIC NASB): a) Image multiplied by 30 times; b) by 1000 times.

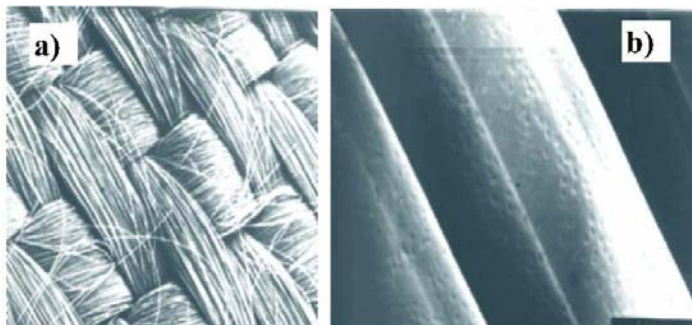


Figure 2. Active carbon fiber "Busofit": a) Image multiplied by 50 times; b) by 1000 times.

"Busofit" is a universal adsorbent, which is efficient to adsorb different gases (H_2 , N_2 , O_2 , CH_4 , and NH_3). Figure 2 shows the texture of the active carbon fiber filament. The carbon fiber refers to microporous sorbents with a developed surface and a complicated bimodal structure. The material can be performed as a loose fibers bed or felt or as monolithic blocks with binder to have a good thermal conductivity along the filament.

In our experiments some samples of activated carbon "Busofit" obtained by the new technology were investigated. The surface area of the commercially available "Busofit" was measured with BET Sorbtometer NOVA and varied from $1140 \text{ m}^2/\text{g}$ up to $1570 \text{ m}^2/\text{g}$. Now it is clear, that methane and hydrogen storage vessels filled with "Busofit" have certain advantages (for example, methane storage capacity near 170 v/v). To be commercially profitable the adsorption storage is required to have at last 150 v/v. It can be considered as a typical microporous adsorbent with pore diameter near 1 – 2 nm and at the same time as material with high gas permeability.

The micropore distribution is performed mostly on the carbon filament surface. Nowadays a program was undertaken to examine the parameters of an active carbon fiber to optimize both the mass uptake of ammonia, methane and hydrogen and the carbon density.

"Busofit" has such advantages as

- high rate of adsorption and desorption;
- uniform surface pore distribution (0.6-1.6 nm);

- small number of macropores (100-200 nm) with its specific surface area 0.5-2 m²/g;
- small number of mesopores with its specific surface area 50 m²/g.

3. Experimental research of texture and hydrogen-sorption capacity for the activated carbon materials

Activated carbon fibers (commercially available “Busofit-AYTM” and modified grades of “Busofit-AYTM”) and granular activated carbon (commercially available and additionally activated at Luikov Institute Porous Media Laboratory) have been used in this work (Table 1).

TABLE 1. Textural characteristics and hydrogen-sorption capacities at 77 K and 0.1 MPa for the researched carbon materials

No	Sorbent	a _v , ml/g	a _H , wt%	S _H , m ² /g	S _{BET} , m ² /g	S _{DR} , m ² /g	V _{DR} , ml/g	V _t , ml/g	R _{DR} , Å
1	Busofit 191-5	199.9	1.76	462	1691	2496	0.887	0.234	49.9
2	Busofit- M2	203.9	1.79	465	1702	2507	0.89	0.43	41.5
3	Busofit- M4	225.1	1.98	536	1715	2547	0.9	0.42	42
4	Busofit- M8	252.9	2.23	571	1939	2985	1.04	0.27	51
5	WAC 97-03	115	1.01	271	715	1050	0.37	0.33	33.4
6	WAC 19-99	172.1	1.51	393	1005	1486	0.53	0.44	41.7
7	WAC 3-00	221.1	1.95	575	1383	2142	0.74	0.22	50
8	207C	209.2	1.84	502	1300	1944	0.69	0.37	41
9	Norit sorbonorit-3	193.8	1.71	458	1361	2044	0.73	0.26	50
10	Sutcliffe	236.6	2.08	527	1925	2864	1.02	0.254	53.6

Remarks: WAC – wood-based active carbon; a_v – volume capacity of hydrogen storage using physisorption, ml/g; a – capacity of hydrogen storage using physisorption, wt%, g/100 g; S_H – BET surface area determined on hydrogen, m²/g; S_{BET} – BET surface area determined on nitrogen, m²/g; S_{DR} – surface area, determined on Dubinin-Radushkevich method, m²/g; V_{DR} – micropore volume, determined on Dubinin-Radushkevich method, ml/g; V_t – mesopore volume, determined on t-method, ml/g; R_{DR} – size of pore, determined on Dubinin-Radushkevich method, Å

Porous texture of the different materials was all characterized using nitrogen (N_2) physisorption at 77 K and up to a pressure of 0.1 MPa. From the nitrogen physisorption data, obtained with the High Speed Gas Sorption Analyser NOVA 1200, the BET-surface area, total pore volume, microporous volume and t-volume were derived. The BET surface area (S_{BET}) is the surface area of the sorbent according to the model formulated by Brunauer et al. [8] for planar surfaces.

The micropore volume is defined as the pore volume of the pores < 2 nm. Microporous volumes calculated from the application of the Dubinin-Radushkevich equation to the N_2 adsorption isotherms at 77 K. The mean pore size of each sample obtained from N_2 adsorption was determined by applying Dubinin-Radushkevich equation. The hydrogen sorption isotherms were measured with the High Speed Gas Sorption Analyser NOVA 1200 at 77 K in the pressure range 0 – 0.1 MPa.

Table 1 summarizes the results of the N_2 and H_2 physisorption measurements of the materials analysed. All samples are highly micro- and mesoporous carbon materials. In our experiments four samples of carbon “Busofit-AYTM” (1 – 4) and three samples of wood-based activated carbon (5 – 7) obtained by new technology were investigated. The activated carbon 207C (8) is made in the Great Britain from coconut shell. Samples 9 and 10 – granular activated carbons, specially developed for effective storage of methane.

According to the offered technology some samples of “Busofit-AYTM” have been prepared with additional activation using thermal processing at high temperature 850 °C. In this way some of the carbon atoms are removed by gasification, which yields a very porous structure. Numerous pores were formed in the carbon material increasing a specific surface area due to the growth of micropore volume. Additional activation of a sample 1 was carried out at the presence of oxygen. As follows from Table 1 the increase of time of activation from two hours until eight hours in an atmosphere of carbon dioxide gas promotes increase to sorption capacity almost in 1.5 times (samples 2 and 4). The atmosphere of carbonic gas appeared more preferably oxygen for growth of a specific surface and sorption capacity – time of activation of samples 1 and 2 was identical. To increase the adsorbent capacity and the bulk density of material we compressed active carbon fiber together with a binder. Briquet “Busofit” disks have a high effective thermal conductivity and a large surface area.

Wood-based carbons (5 – 7) were produced by controlled pyrolysis of waste wood by the Institute of General and Inorganic Chemistry NASB and additional activation (WAC 3-00).

As seen in Table 1, the greatest values of a surface area and micropore volume among carbon fibrous materials has “Busofit-M8”; among wood-based activated carbons it is stand out “WAC 3-00”, granular carbons – “Sutcliff”.

The approach of research institutes AGLARG [9] was used for an operative estimation of gas sorption capacity for carbon sorbents. According to it micropore volume and the specific surface area have been chosen as determining parameters. To obtain the function approximating dependence of hydrogen sorption capacity on carbon materials from value of a specific surface area (at pressure 0.1 MPa and temperature 77 K), we used our experimental data (Table 1) and an experimental database (Table 2) of group of institutes - Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University [10].

A test matrix of about 20 different carbon samples, including commercial carbon fibers and fiber composites, graphite nanofibers, carbon nanowebs and single walled carbon nanotubes was assembled. The sorbents were chosen to represent a large variation in surface areas and micropore volumes. Both non-porous materials, such as graphites, and microporous sorbents, such as activated carbons, were selected. Characterization via N₂ adsorption at 77 K was conducted on the majority of the samples; for this a Quantachrome Autosorb-1 system was used. The results of the N₂ and H₂ physisorption measurements are shown in Table 2. In the table CNF is used to designate carbon nanofibers, ACF is used for activated carbon fibers and AC for activated carbon.

TABLE 2. Textural characteristics and hydrogen-sorption capacities at 77 K and 0.1 MPa for carbonaceous materials [10]

No	Sorbent	S _{BET} , m ² /g	V _{DR} , ml/g	a _v , ml/g	a _{v, meso} , ml/g	a _{v, micro} , ml/g
1	Synthetic graphite	7	0.00	0	0	0
2	Large-diameter CNF	49	0.01	6	2	4
3	Activated graphite 100	119	0.02	14	6	8
4	Medium-diameter CNF1	120	0.00	12	11	1
5	ACF 400	883	0.34	143	1	142
6	ACF 1200	899	0.37	184	1	183
7	AC Norit 990721	988	0.43	142	2	140
8	AC Norit ROZ 3	287	0.05	36	6	28
9	Activated graphite 300	287	0.05	36	16	19
10	Medium-diameter CNF2	65	0.00	7	7	0
11	AC Norit SX 2	841	0.27	150	17	133
12	ACF 500	988	0.40	142	15	127
13	AC Norit UOK A	1195	0.47	188	10	178
14	AC Norit SX 1	922	0.31	168	18	150
15	AC Norit SX 1G AIR	1030	0.36	171	16	155
16	AC Norit GSX	933	0.26	161	27	134
17	AC Norit SX plus	1051	0.35	165	21	144
18	AC Norit SX 1 G	1176	0.40	187	20	167
19	AC Norit 990293	2029	0.92	238	7	231
20	AC Norit Darco KB	1462	0.42	146	54	92
21	Hyperion CNF	238	0.00	22	22	0

For carbon samples we have found linear relationship between BET surface area and volume sorption capacity of hydrogen at 77 K and 0.1 MPa as:

$$a_v = 0.0783 S_{BET} + 84.02 \tag{1}$$

Figure 3 shows all experimental data and variants of approximation. It is possible to see that our linear correlation fairly good describes all results except for the literature data which correspond to materials with low values hydrogen sorption capacity ($a_v < 50$ ml/g).

Influence of micropore volume on sorption capacity of hydrogen for various carbon materials under the chosen conditions (77 K, 0.1 MPa) is well described by the following linear correlation:

$$a_v = 119.12V_{DR} + 115.41 \quad (2)$$

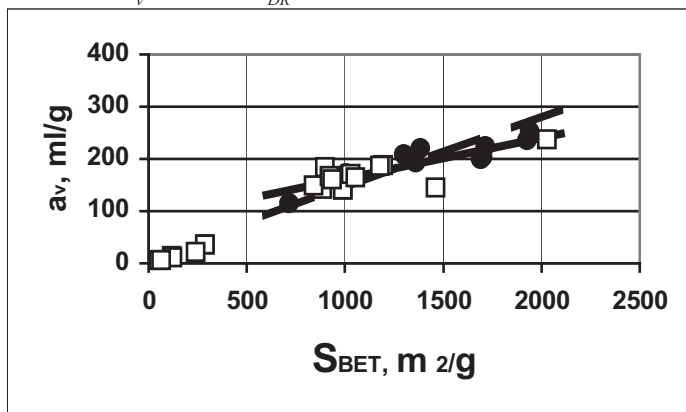


Figure 3. Volume capacity of hydrogen storage for carbon sorbents vs. BET surface area at pressure 0.1 MPa and 77 K: ● – experimental data (Table 1), a continuous line – the linear approximation obtained by authors; □ – experimental data (Table 2), a dashed line – the linear approximation given in [10].

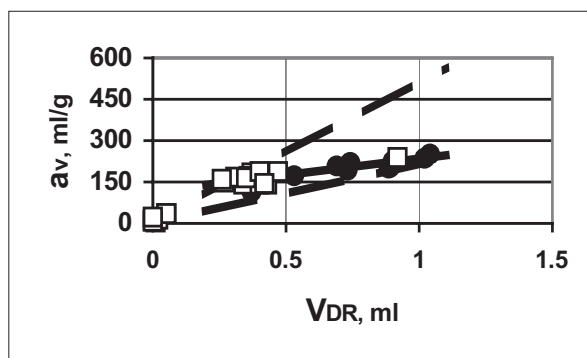


Figure 4. Volume capacity of hydrogen storage for carbon sorbents vs. micropore volume (determined on Dubinin-Radushkevich method) at pressure 0.1 MPa and 77 K: ● – experimental data (Table 1), a continuous line – the linear approximation obtained by authors; □ – experimental data (Table 2), a dashed line – the linear approximation given in [10].

From Fig. 4 it can be concluded that this correlation does not apply to the carbon samples with low values sorption capacity of hydrogen ($a_v < 50$ ml/g). "Hydrogen" sorbent should have maximum high value of a specific surface area and maximum narrow distribution of micropores.

As follows from Table 1, sorbents "Busofit-M8", "Sutcliff" have micropore volume more than 1 ml/g. They are also the best storage systems for hydrogen (accordingly 253 ml(STP)/g and 237 ml(STP)/g) due to physisorption. Our results demonstrate that a large capacity of adsorbed hydrogen by physisorption under chosen conditions is obtained with sorbents containing a large volume of micropores and a high BET surface area. Optimization of sorbent and sorption conditions is expected to lead to storage capacity of 500–600 ml(STP)/g, close to targets set for mobile applications.

4. The analysis of isotherms of hydrogen sorption by carbon materials at medium pressures

4.1. EXPERIMENTAL SET-UP

The analysis of isotherms of gas at the temperature interval 233 – 293 K and pressure interval 0.1 – 6 MPa was realized by the gravimetric control of the sample (200–400 g) during adsorption/desorption cycle. The experimental set-up is shown in Fig. 5.

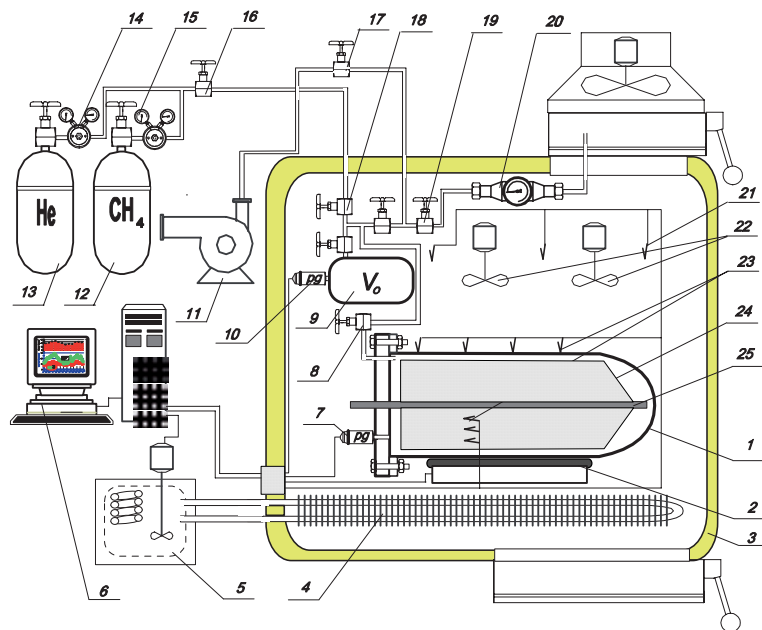


Figure 5. Experimental apparatus: 1 – AG cylinder, 2 – electronic balance, 3 – insulated chamber, 4 – heat exchanger, 5 – thermostat, 6 – computer with software, 7, 10 – pressure sensors, 8, 16 – 19 – valves, 9 – calibrated volume, 11 – vacuum pump, 12 – hydrogen vessel, 13 – helium vessel, 14, 15 – reducer, 20 – flow meter, 21, 23 – thermocouples, 22 – fans, 24 – sorbent bed, 25 – heat exchanger.

The full amount of the adsorbate was measured. The cylindrical experimental rig of 47 mm inner diameter and 540 mm length was used to simulate full-scale conditions of the experiment. This experimental rig was made from the stainless

steel and served as a simulator of the real vessel in the ratio 1:50. Thermocouples were attached to the sample through the sorbent bed (12.5 mm thick). Pressure sensor was used for pressure measurements in the experimental chamber.

4.2. SORPTION ISOTHERMS FOR A HIGH SURFACE ACTIVATED CARBONS

The rate of the adsorption/desorption of different gases (methane, hydrogen) on the surface of “Busofit” can be evaluated by the isotherms analysis at different temperatures of the sorbent bed. In order to study the sorption capacity of the adsorbent it is necessary to know the quantity of gas adsorbed on each point of the cycle. There is a general need to have a good fit of experimental isotherms and temperature and to extrapolate some isotherms beside the experimental field. For the carbon fiber “Busofit” the approach of Dubinin is well adapted and allows linking quite simply the physical properties of “Busofit” to the capacity of adsorption of the carbon fiber. Methane isotherms evolution during the cycle of adsorption/desorption of “Busofit AYTМ” is presented in [11, 12]. Based on these data we can conclude that “Busofit-AYTМ” is competitive to best activated carbons with methane adsorption capacity 113 – 135 g/g at 273 K.

As an example, Fig. 6 shows the experimental isotherms of the adsorption and desorption of hydrogen on carbon fiber “Busofit-M8” and wood-based activated carbon “WAC 3-00” at the nitrogen temperature. Absence of an appreciable hysteresis confirms that reversible physisorption exclusively takes place with all investigated materials.

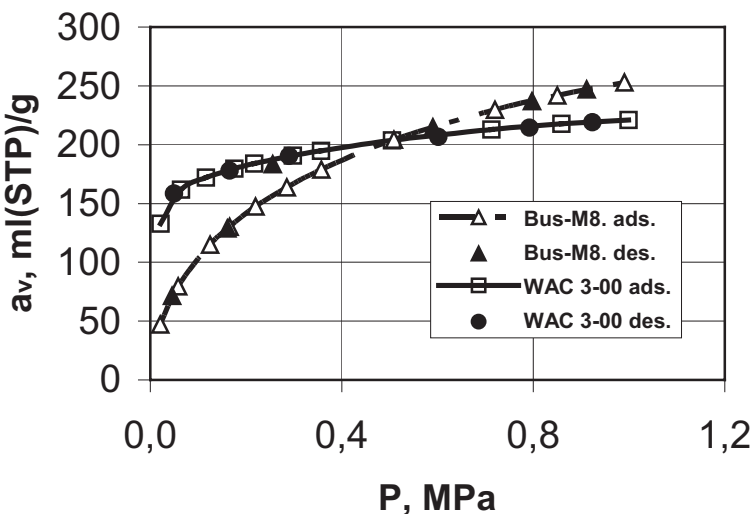


Figure 6. Isotherms of hydrogen adsorption and desorption on carbon materials at temperature 77K, measured by the High Speed Gas Sorption Analyser NOVA 1200.

Physisorption on microporous carbons can be described with the Dubinin-Radushkevich equation [13]

$$a_{eq} = \frac{W_0}{v_a} \exp \left\{ - \left[\frac{R_\mu T \ln(P_{sat} / P)}{E} \right]^2 \right\}. \tag{3}$$

The theory of microporous volume filling, worked out by Dubinin, is widely used for quantitative characteristic of adsorptive properties and basic varieties of porous structure. Equilibrium state equation (3) includes the saturation pressure P_{sat} . Since the hydrogen sorption isotherms are measured within the temperature and pressure intervals comprising the regions of supercritical states of the adsorptive ($T_{cr} = 33.24 \text{ K}$ $P_{cr} = 1.298 \text{ MPa}$), the notion of saturation pressure loses its physical meaning. In the work [14] the saturation pressure is determined by the formula:

$$P_{sat} = P_{cr} (T / T_{cr})^2 \tag{4}$$

As a results of the experiments, we obtained hydrogen sorption isotherms for different carbon materials and empirical coefficients for the Dubinin-Radushkevich equation (5), presented in Table 3.

TABLE 3. The empirical coefficients of Dubinin-Radushkevich equation for hydrogen sorption on the carbon materials

Material	W_0 , ml/g	E, J/g
Busofit-M2	369	1783
Busofit-M4	376	1922
Busofit-M8	482	1710
Sutcliffe	453	1699
WAC 3-00	270	3782
207 C	343	1969

With the purpose of a choice of the most suitable sorbent of hydrogen, isotherms (Fig. 7) of studied materials were compared at a level of pressure 3.5-6 MPa, representing practical interest for development of onboard storage system. It is obvious, that the best sorbent in the field of nitrogen temperature – the activated fiber "Busofit-M8", having major effective porosity (0.78), bulk density of 500 kg/m³ and an advanced surface area (2985 m²/g).

At pressure 6 MPa "Busofit-M8" reaches storage capacity up to 482 ml/g. Apparently, that 8-hours post-treatment of a carbon fiber by carbonic gas enhanced both microstructural, and the surface characteristics of the original "Busofit". As a result, the hydrogen sorption of a carbon fiber at cryogenic temperatures was improved almost twice, in comparison with samples "Busofit-M2" and "Busofit - M4" whose activation was prolonged a smaller time. From the analysis of physisorption isotherms (Fig. 7) follows, that the wood-based carbon "WAC 3-00" with the greater specific surface area (S_{BET} =1382 m²/g) immerses the smaller

amount of hydrogen and its isotherm lays below an isotherm of carbon 207C with a specific surface area equal to 1300 m²/g. The similar "abnormal" behaviour can be explaining different pore size distributions of carbon materials [14].

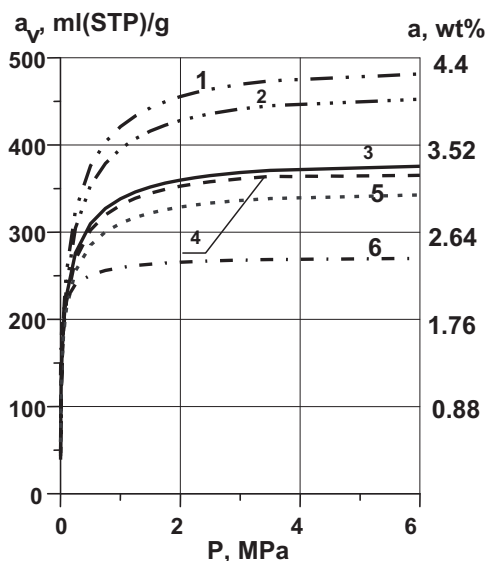


Figure 7. Hydrogen sorption isotherms for the temperature 77 K and different carbon materials: 1 – “Busofit-M8”, 2 – “Sutcliff”, 3 – “Busofit-M4”, 4 – “Busofit-M2”, 5 – 207 C, 6 – “WAC 3-00”.

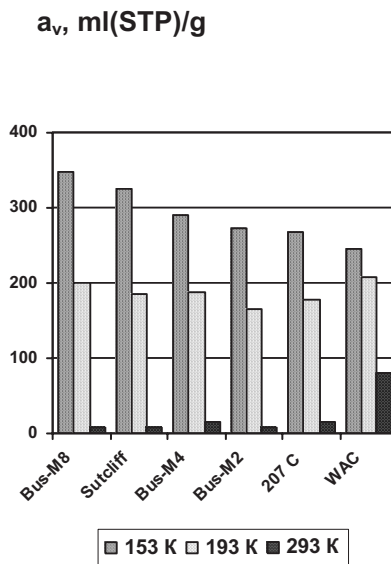


Figure 8. Volume capacity of hydrogen storage using physisorption at pressure 6 MPa for active carbon materials and different temperatures.

A summary of the results on volumetric capacity of storage of hydrogen for the investigated materials is given on Fig. 8. It is observed that the H₂ uptakes are very low at room temperature and pressure 6 MPa for all carbon samples, but the wood-based material of large surface area has the best sorption characteristics – storage capacity equal of 80 ml(STP)/g.

The influence of temperature can be seen on Figs. 8–9. The storage capability is increasing for lower temperatures. Figure 9 compares the behaviour of the adsorption isotherms at different temperature levels for two of the more promising samples: steam activated “Busofit-M8” and wood-based carbon “WAC 3-00”. The shape of the isotherms in the two cases is dissimilar. The isotherms for the 77 and 153 K exhibit a classical type 1 isotherm shape indicating a microporous material. The isotherms at room temperature exhibit a much less pronounced curvature (more like type II isotherm). As is seen from plots (Fig. 9) experimental data fit the calculated adsorption values (Dubinin-Radushkevich equation) with an error sufficient for practical purposes.

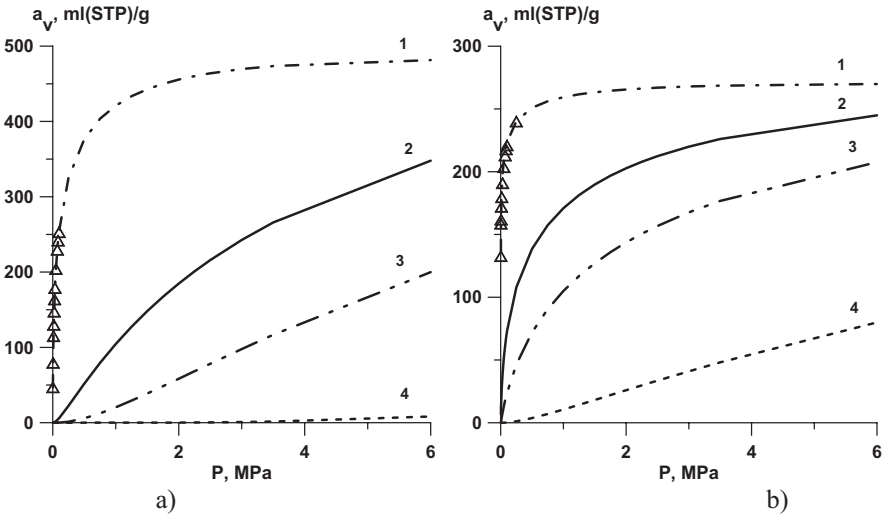


Figure 9. Hydrogen adsorption isotherms for active carbon fiber “Busofit-M8 ” (a), wood-based carbon “WAC 3-00” (b) and different temperatures (1 – 77, 2 –153, 3 – 193, 4 – 293 K): experimental data – points, calculated data (Dubinin-Radushkevich equation) – lines.

5. Heat and mass transfer in the sorbent bed

Carbon material can be used as a compact "sandwich" with cylindrical or flat heat pipes, applied as thermal control systems. The dynamic mathematical thermal model of the sorbent bed (Fig. 10) has following constituents [12]:

- 1) Dubinin and Radushkevich equation (3) of the state of gas;
- 2) the equation of energy:

$$r(\varepsilon C_g + \rho C + \rho a C_a) \frac{\partial T}{\partial \tau} + rcv C_g \frac{\partial T}{\partial r} = \frac{\partial}{\partial r} \left(r \lambda \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(r \lambda \frac{\partial T}{\partial z} \right) + r q_{st} \rho \frac{\partial a}{\partial \tau}, \quad (5)$$

where the isosteric heat of desorption is: $q_{st} = R_\mu T \left[\frac{\partial \ln P}{\partial \ln T} \right]_{a=\text{const}}$; (6)

- 3) the equation of continuity:

$$r \frac{\partial}{\partial \tau} (\varepsilon c + \rho a) + \frac{\partial}{\partial z} (rcv) = 0; \quad (7)$$

- 4) the equation of kinetic of sorption:

$$\frac{da}{d\tau} = K_{so} \exp \left(-\frac{E}{R_\mu T} \right) (a_{eq} - a), \quad (8)$$

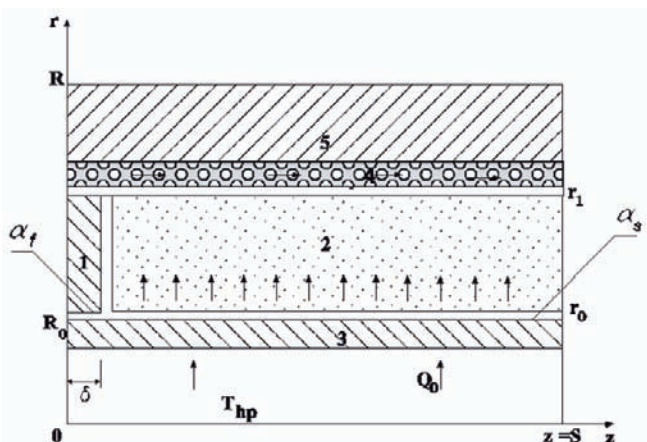


Figure 10. Diagram of the calculated element of the SSH: 1 – fin; 2 – sorbent; 3 – shell of the heating element; 4 – channel for gas discharge formed by the perforated tube and the cylinder body; 5 – cylinder body.

where $K_{s0} = 15D_{s0} / R_p^2$, R_p – radii of the particle. D_{s0} – constant necessary to determine the coefficient of a surface diffusion, $D_s = D_{s0} \exp[E / (R_\mu T)]$

The solution was found for the fixed gas flow from the SSH vessel

$$2\pi \frac{d}{d\tau} \int_0^{L_1} \int_0^1 (\varepsilon c + \rho a) r dr dz = -g / N \quad (9)$$

with boundary conditions:

$$P|_{\tau=0} = P_0; \quad T(r, z)|_{\tau=0} = T_0(r, z) = T_{env}; \quad (10)$$

$$\left. \frac{\partial T}{\partial z} \right|_{z=0} = 0, \quad \left. \frac{\partial T}{\partial z} \right|_{z=S} = 0; \quad -\lambda \left. \frac{\partial T}{\partial r} \right|_{r=R} = \alpha_{env} (T - T_{env}), \quad (11)$$

$$-\lambda \left. \frac{\partial T}{\partial r} \right|_{r=R_0} = \frac{Q_{hp}}{2\pi R_0 S N}, \text{ or } T|_{r=R_0} = T_{hp}, \quad (12)$$

where Q_{hp} – heat flow used to heat one cylinder of the vessel, T_{hp} – gas vessel wall temperature.

The first condition (12) corresponds to the situation where the power Q_{hp} is known, and the second condition corresponds to the situation where the heating power is not limited and the temperature T_{hp} is set. This temperature is maintained at the inner surface of the heat pipe due to the contact of its evaporation zone with a large heated body, such as an engine. To solve the set of equations (3, 5–8) with boundary conditions (10–12) the method of finite elements was chosen.

The suggested simple model gives us a possibility to obtain the field of temperature and gas concentrations during charge-discharge (adsorption/desorption) procedures of the gas vessel. A set of calculations was performed for the high-surface area activated carbon fiber “Busofit-M8” and wood-based carbon “WAC 3-00” as promising gas sorption materials to design a hydrogen storage system. Figure 11 shows the plots of the volume storage density of hydrogen in the vessel (50 l) as a function of the temperature. It is evident that it is necessary to take into account the presence of the compressed gas in the adsorbed storage system at pressures 3.5-6 MPa, the compressed fraction can be measured up to 30 – 50 %. The maximum volume storage density of hydrogen was 380 v/v at 77 K and 6 MPa for “Busofit”. It is important, that the whole amount of storage gas was about 180 v/v at 195 K. However, the “WAC 3-00” sample ensured the value 120 v/v at 273 K.

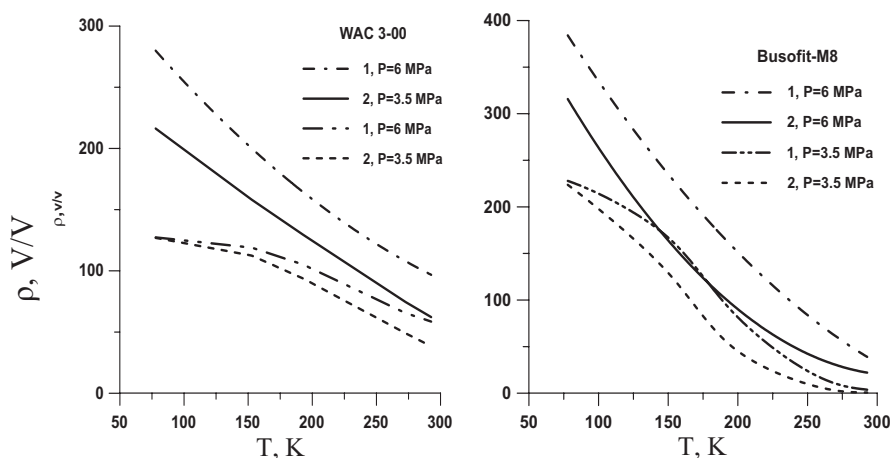


Figure 11. Volume storage density of hydrogen (1 – the adsorbed and compressed gases; 2 – the adsorbed phase) vs. temperature for different pressure: $P = 6 \text{ MPa}$ and 3.5 MPa .

6. Heat pipe based heat exchangers

The efficient system to perform a sorbent bed thermal control during its charging/discharging is heat pipe based heat exchangers. Sorbents can be used as a compact sandwich with flat or cylindrical heat pipes being in good thermal contact with the surrounding or source of energy (for example, gas flame, electric heater). Various types of heat pipes: conventional heat pipes, heat pipe panels, loop heat pipes, vapour-dynamic thermosyphons and other two phase evaporation/condensation heat transfer technologies and equipment were developed and used for sorbent bed thermo control at Heat and Mass Transfer Institute. Choosing of appropriate type of heat pipes is complex problem, which depends on working conditions and limitations, temperature range, source of energy, necessity of recovery, cost etc.

Heat pipes can easily be implemented inside sorption storage vessels. They are the most convenient thermal control devices for the solid and liquid sorption machines due to its flexibility, high thermal efficiency, cost-effectiveness, reliability, long operating life, simple manufacturing technology.

Conventional heat pipes (Fig. 12) are convenient as heat transfer devices for sorption bed layer thermal control [15].

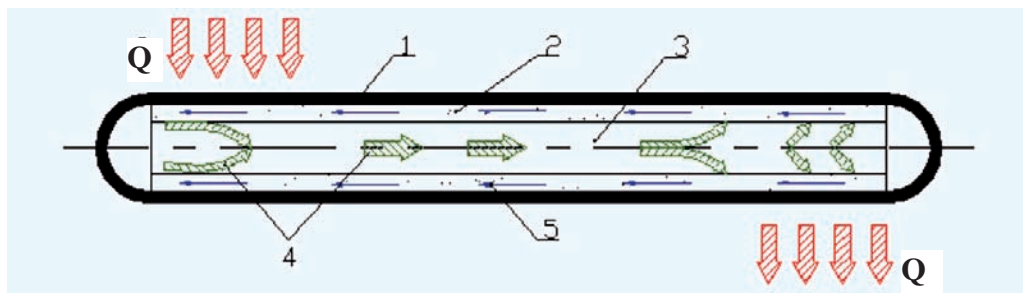


Figure 12. Conventional heat pipes schematic: 1 – envelope, 2 – porous wick, 3 – vapour channel, 4 – vapour, 5 – liquid.

A very important feature of heat pipe (HP) is the ability to transport a large amounts of energy over the length of heat pipe with a small temperature drop by means of liquid evaporation at the heat pipe evaporator (heat source) and vapour condensation at the condenser (heat sink) and liquid movement in the opposite direction inside a wick by capillary force. Essential is a possibility to change the direction of a heat flow along the heat pipe in time and to use heat pipes for cooling and heating alternatively.

Thermosyphons are a simple devise for thermal control of sorbent bed. Very suitable new design of thermosyphon, so called **vapour-dynamic thermosyphon** (Fig. 13), was especially developed for thermal regulating of continuous long horizontal objects.

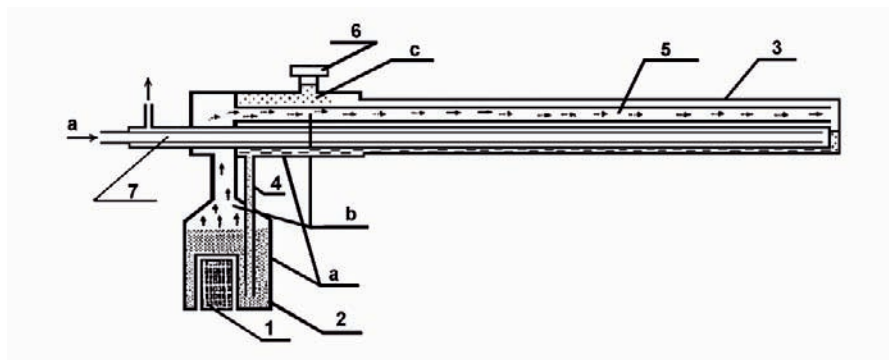


Figure 13. Water/SS "vapour-dynamic" thermosyphon: 1-electric heater; 2-boiler; 3-condenser; 4-feeding liquid tube; 5-vapour passage ; 6-trap for NCG (on the top of additional condenser); 7- water heat exchanger; a - water; b -vapour; c – NCG.

The advantages of this thermosyphon are [16]:

- 1) high heat transfer performance duty vapour and liquid flows separation, there are no interface friction losses;
- 2) low thermal resistance because of high velocity vapour flow in the gap between the condenser tubes make thin the liquid film on the condensing surface, enhancing heat transfer with condensation;
- 3) vapour flow in the gap evacuated the non-condensable gases to additional condenser (small volume at the end of vapour path from main condenser), that means the ability work with non-condensable gas presence;
- 4) the ability to transport of energy in horizontal direction, which is difficult to realise by conventional thermosyphons.

Vapour-dynamic thermosyphons are capable to transport heat up to 10 kW and more for the distance some meters, which is difficult to realise by conventional thermosyphons, horizontally disposed.

Capillary pumped loops are attractive alternative for heat regulation [15]. The capillary pumped evaporator is used instead of the boiler. A capillary pumped evaporator is more flexible with the point of view of its orientation in space and is more compact. This principal difference of vapour generating gives the possibility to use the evaporator in higher level that condensers.

For some applications flat **heat pipe panels** (HPP) have advantages over conventional cylindrical heat pipes, such as geometry adaptation, ability for localized heat dissipation and the maintenance of an entirely flat isothermal surface (Fig. 14). The liquid-vapour interface formed in capillary channels inside the heat pipe panel is capable to generate self-sustained thermally driven oscillations. Thin layer (several mm) of the sorbent between mini-fins on the outer side of the heat pipe panel ensures an advanced heat and mass transfer during the cycle adsorption/desorption.

This device is filled partially with working fluid. The flow instabilities inside of this device are produced due to the heat input in one part of it and heat output from the another part by heating multi-channels ($H = 2\text{mm}$, $L = 5\text{ mm}$) at one end and simultaneously cooling the other end thus resulting in pulsating fluid. This heat input and output stimulates a heat transfer, as a combination of sensible and latent heat portions. The flow instabilities are a superposition of various underlying effects.



Figure 14. Heat pipe panels (pulsating heat pipes) and cylindrical heat pipes for sorbent bed thermal control.

In our experiments as an experimental set-up an aluminium multi-channel panel was chosen. The main parameters of flat aluminium heat pipe panel, developed in the Luikov Institute are: HPP width -70mm, HPP height - 7 mm, HPP length – 700 mm, evaporator length - 98 mm, condenser length – 500 mm, mass- 0, 43 kg. Propane was applied to fill the HPP and it is interesting as a working fluid with the point of view of its compatibility with all heat pipe envelopes and wick materials (aluminium, steel, stainless steel, copper, AL_2O_3 , etc).

7. Conclusions

- Original hydrogen sorption capacity and structural data for carbon materials were obtained. Empirical formulas for predicting of hydrogen sorption by carbons were offered.
- To improve the parameters of the gas storage systems the technology of carbon sorption capacity enhancement including additional activation was developed.
- The application of heat pipes in gas accumulator enables one to control the temperature of sorbent bed and provide optimum operational conditions.
- Different heat pipe devices for thermal control (cylindrical copper pipes with metal sintered powder as a wick, flat heat pipe panels, loop heat pipes with capillary pumped evaporators, vapour-dynamic thermosyphons and others) were developed and can be successfully integrated in sorption storage vessels.
- A simple theoretical model of cylindrical AG vessel with internal finned heater/cooler (HP based) was suggested.
- Application of sorption material based on activated carbon in solid sorption storage vessels has good perspective for developing a new type of gas storage systems. The designed AGS systems and modified carbon sorbents (BUSOFIT-M8, WAC 3-00) are perspective for the hydrogen storage and for two-fuel automobile.

Acknowledgments

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Nomenclature

a , current, or nonequilibrium, adsorption, kg/kg; c , density of free gas, kg/m³; C , specific mass heat of the sorbent skeleton, J/(kg-K); C_g , specific mass heat of the free gas, J/(kg-K); C_a , heat capacity of the adsorbed methane, J/(kg-K); E , activation energy, J/kg; G , mass flow rate of the gas flowing out of the cylinder, kg/sec, g/sec; g_i , mass flow rate of the gas flowing out of the calculated cell of the cylinder, kg/sec; K_{so} , preexponential factor in the approximate kinetic equation; m , dynamic coefficient of filling the cylinder; m_e , unwithdrawn gas mass; M , mass of the gas in the cylinder, kg; M_i , mass of the gas in the calculated cell, kg; N , number of calculated cells in the cylinder; P , pressure, Pa; q_{st} , heat of phase transition, or isosteric sorption heat, J/kg; Q_{hp} , power of heating of the entire cylinder, W; r and z cylindrical coordinates, m; R , outside radius of the cylinder shell, m; R_o , inside radius of the heating-element shell, m; r_o and r_i , inside and outside radii of the annular layer of the sorbent, m; R_u , gas constant, J/(kg-K); R_p , mean radius of the particles, mm; T_{hp} , temperature at the inner surface of the

heating-element shell, K, °C; $2S$, finning step, m, mm; T , temperature, K, °C; $\bar{T}$, mean temperature of the sorbent layer, K; v , component of the velocity vector, m/sec; v_a – specific volume of adsorbed media; V_a , partial molar adsorption volume; V_g , molar gas-phase volume; z_g , coefficient of gas compressibility; α , coefficient of heat transfer, W/(m²-K); ϵ , porosity determined as a part of the volume occupied by the free gas (not bound by adsorption); 2δ , fin thickness, m, mm; λ_{eff} , effective thermal conductivity of the sorbent layer, W/(m-K); ρ_s , density of the sorbent skeleton, kg/m³; ρ , total density of the free and adsorbed gases in the cylinder, kg/m³; ρ_v , volume density of storage, nm³/m³; τ , time, sec. **Subscripts.** eq, equilibrium conditions; a, adsorbate; cr, critical state; e, finite value; env, environment; hp, heat pipe; 0, initial value; s, sorbent; f, fin; t, transfer.

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INFLUENCE OF HYDROGEN ON MAGNETIC AND MAGNETOELASTIC PROPERTIES OF $\text{Lu}_2\text{Fe}_{17}$ SINGLE CRYSTAL

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Abstract. Magnetic properties of the $\text{Lu}_2\text{Fe}_{17}$ single crystal and its hydride $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ have been studied by means of magnetization and magnetostriction measurements. An unusual magnetic behavior with two magnetic phase transitions has been observed in the host compound. It was found that hydrogenation leads to suppression of antiferromagnetism and induction of the ferromagnetic state with a high Curie temperature ($T_C = 393$ K). The hydrogenation exerts a significant influence on magnetoelastic properties of the $\text{Lu}_2\text{Fe}_{17}$ single crystal: a thermal expansion along the c-axis becomes positive, magnetostrictive deformations decrease.

Keywords: rare-earth compound, hydride, magnetization, magnetic ordering temperature, magnetostriction, thermal expansion coefficient

1. Introduction

The R_2Fe_{17} compounds belong to the most interesting group of rare earth – iron intermetallics which attracts much attention of investigators [1, 2]. They crystallize in two related types of crystal structure: the rhombohedral $\text{Th}_2\text{Zn}_{17}$ and hexagonal $\text{Th}_2\text{Ni}_{17}$, when R is a light or heavy rare earth metal, respectively. A characteristic feature of the R_2Fe_{17} compounds is that their magnetic properties strongly depend on the unit cell volume and interatomic distances [3]. It results in a substantial change of the magnetic ordering temperature T_C under the hydrostatic pressure [4, 5]. The most impressive effect was a considerable increase of Curie temperature (by approximately 200 K) upon introduction of nitrogen atoms into the crystal lattice of $\text{Sm}_2\text{Fe}_{17}$ [6, 7], which is accompanied by an appearance of the strong uniaxial magnetocrystalline anisotropy.

Among the R_2Fe_{17} compounds the $\text{Lu}_2\text{Fe}_{17}$ compound is less studied because of difficulty to obtain enough large high-pure single crystals. It has been established [8, 9] that small uncontrolled impurities lead to suppression of the antiferromagnetic state and shift T_C toward the higher temperatures. Magnetic properties of the $\text{Lu}_2\text{Fe}_{17}$ single crystal provide valuable information about magnetism of the iron sublattice in the R_2Fe_{17} compounds. The purpose of the present work is to investigate the influence of hydrogenation on magnetic and magnetoelastic properties of the $\text{Lu}_2\text{Fe}_{17}$ single crystal.

2. Experimental

The ingot $\text{Lu}_2\text{Fe}_{17}$ of 7 g mass was prepared by arc melting stoichiometric mixtures of pure (99.9%) elements in a tetra-arc furnace on a rotating water-cooled copper crucible under a protective argon atmosphere. The alloy button was turned over and then kept in melting state for about 1 hour before pulling crystals in order to ensure a perfect homogeneity. The single crystal was grown by Czochralski method using a tungsten wire as a seed under 10 mm/hour pulling speed. The back Laue patterns were used to check the single-crystal state and to orient the crystal for cutting the samples. The composition microprobe analysis was performed using a JXA-733 (JEOL) electron microscope.

Hydrogenation was performed in a stainless steel autoclave under the hydrogen gas pressure of 1 MPa at 150°C. The amount of absorbed hydrogen has been determined volumetrically. The hydrogen concentration was near to 1.5 H atom per formula unit: $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$.

The magnetization measurements were performed in magnetic fields up to 11 kOe at temperatures 1.5–500 K using a SQUID-magnetometer. The magnetostriction and thermal expansion measurements were made by the strain-gauge method on the plate-like samples with the linear sizes of $7 \times 5 \times 1.5$ mm in the temperature range from 77 to 400 K and magnetic fields up to 12 kOe.

3. Results and Discussion

Figure 1 shows the temperature dependence of magnetization $\sigma(T)$ for the $\text{Lu}_2\text{Fe}_{17}$ single crystal measured along the a-axis in magnetic field of 0.1 kOe. There are some features on the $\sigma(T)$ curve: i) a sharp slump at $T = 180$ K (the ferromagnetic (FM) – antiferromagnetic (AFM) transition), which is accompanied by a considerable hysteresis (~ 50 K) and ii) a weak maximum typical for the AFM – PM (paramagnetic) transition with the Néel temperature $T_N = 278$ K, which agrees well with the literature data [10, 11].

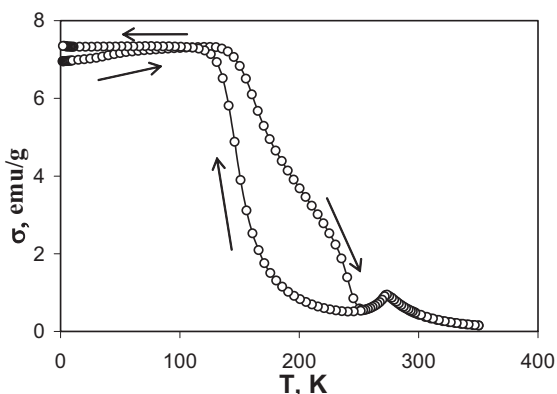


Figure 1. Temperature dependence of magnetization measured along the a-axis in magnetic field of 0.1 kOe for the $\text{Lu}_2\text{Fe}_{17}$ single crystal.

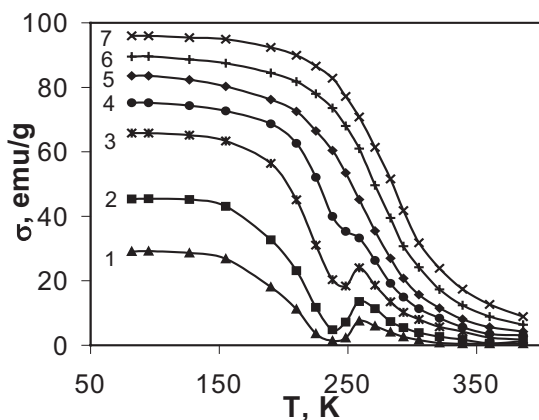


Figure 2. Temperature dependencies of magnetization of the $\text{Lu}_2\text{Fe}_{17}$ single crystal measured in different magnetic fields of: 1 – 0.5 kOe, 2 – 1 kOe, 3 – 2 kOe, 4 – 3 kOe, 5 – 4.5 kOe, 6 – 7.5 kOe, 7 – 11 kOe.

Measurements of the field and temperature dependencies of magnetization ($\sigma(H)$ and $\sigma(T)$) were performed in order to show the transformation of the AFM state into the FM state by an external field. Figure 2 shows the temperature dependence of magnetization $\sigma(T)$ measured along the *a*-axis of the $\text{Lu}_2\text{Fe}_{17}$ single crystal in different magnetic fields. A metamagnetic transition from AFM to the FM state becomes apparent in magnetic fields up to 3.3 kOe. The temperature dependence of the critical field $H_{\text{cr}}(T)$ is shown in the Fig. 3. As one can see from the Fig. 3, H_{cr} rises with the temperature increase, has a narrow maximum and abruptly decreases approaching the Néel temperature. Thus, the magnetic field of $H > 3.3$ kOe suppresses the AFM state in the $\text{Lu}_2\text{Fe}_{17}$ compound.

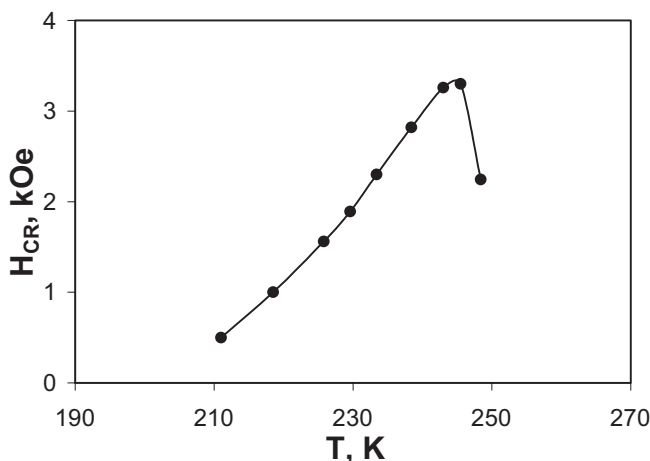


Figure 3. Temperature dependence of the critical field $H_{\text{CR}}(T)$ for the $\text{Lu}_2\text{Fe}_{17}$ single crystal.

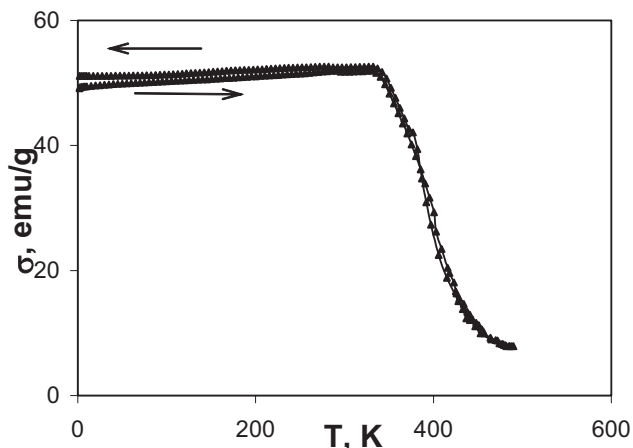


Figure 4. Temperature dependence of magnetization measured along the a-axis in the magnetic field of 0.5 kOe for the $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ single crystal.

Hydrogen also suppresses the AFM and induces the FM state in $\text{Lu}_2\text{Fe}_{17}$. Hydrogenation increases the Curie temperature which reaches the value of $T_C = 393$ K (see Fig. 4).

Assuming, that an increase of Curie temperature of $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ is mainly caused by the increase of exchange integrals as a result of the unit cell volume expansion upon hydrogen atoms incorporation, we calculated the change of T_C according to the following relation:

$$\Delta T_C^{\text{calc}} = -\frac{T_C}{k} \frac{\Delta V}{V} \frac{d \ln T_C}{dp},$$

where k is the compressibility.

We have used an experimental data for $\Delta V/V = 1.02\%$, $k = 1.05 \cdot 10^{-11} \text{ Pa}^{-1}$ and $d \ln T_C / dp = -8.4 \cdot 10^{-11} \text{ Pa}^{-1}$ estimated earlier for $\text{Lu}_2\text{Fe}_{17}$ [12]. It was found however, that the calculated value of $\Delta T_C^{\text{calc}} = 22.5$ K is smaller than the observed one $\Delta T_C^{\text{exp}} = 115$ K. Recently, for $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.01}$ we have obtained a better agreement between the experimental $\Delta T_C^{\text{exp}} = 12$ K and calculated $\Delta T_C^{\text{calc}} = 8.5$ K values [13]. We also tried to calculate an increase of Curie temperature in the $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ hydride in terms of the spin fluctuations theory using a method proposed by Grebennikov et al. [14, 15]. In this case we have got $-\Delta T_C^{\text{calc}} = 175$ K. We conclude that the localized magnetic moments model describes the ΔT_C^{calc} changes in $\text{Lu}_2\text{Fe}_{17}\text{H}_x$ hydrides well when the hydrogen concentration x is about 1 at.H/f.u. Unfortunately, the increase of Curie temperature for $\text{Lu}_2\text{Fe}_{17}\text{H}_x$ with $x > 1$ at.H/f.u. could not be accurately calculated neither within the localized nor in the itinerant electrons models.

Thermal expansion $\Delta l/l$ of the $\text{Lu}_2\text{Fe}_{17}$ compound was investigated earlier [3] in the wide temperature range of 4–1000 K. A negative thermal expansion was observed for the c parameter. In this paper we carried out measurements of $\Delta l/l$ along c -axis in the 77–300 K temperature range. The sample was placed in the external magnetic field of 0.1 kOe applied along the a -axis. We found that the

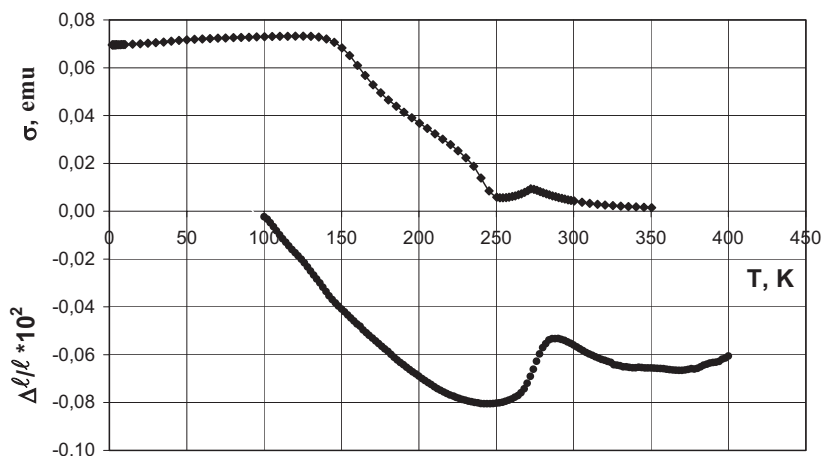


Figure 5. Temperature dependencies of magnetization (on top) and thermal expansion $\Delta l/l$ (on bottom) measured in magnetic field of 0.1 kOe for the $\text{Lu}_2\text{Fe}_{17}$ single crystal.

features observed on the thermal expansion curve $\Delta l/l$ correlate with the features observed on the magnetization curve $\sigma(T)$ at $H=0.1$ kOe (see Fig. 5).

Figure 6 shows the temperature dependencies of the thermal expansion coefficients $\alpha(T)$ for the $\text{Lu}_2\text{Fe}_{17}$ single crystal and its hydride $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$. As can be seen, $\alpha(T)$ of the host compound is negative at $T < 245$ K, then it changes its sign and rises sharply. The maximum of $\alpha(T)$ is observed at $T_N = 278$ K. A positive thermal expansion along the c -axis is observed for $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ in the whole temperature range investigated. Thus, our investigations showed that hydrogenation exerts a significant influence on magnetoelastic properties of $\text{Lu}_2\text{Fe}_{17}$.

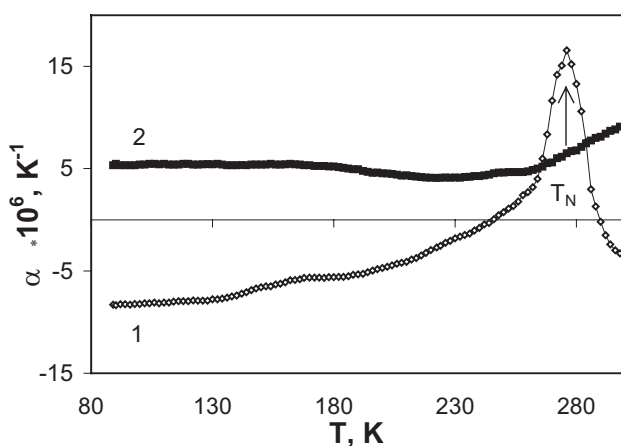


Figure 6. Temperature dependencies of the linear thermal expansion coefficient $\alpha(T)$ along the c -axis of the $\text{Lu}_2\text{Fe}_{17}$ single crystal (1) and its hydride $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ (2).

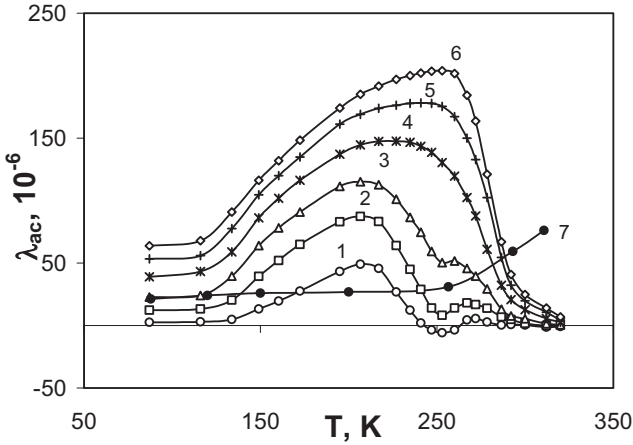


Figure 7. Temperature dependencies of λ_{ac} for the $\text{Lu}_2\text{Fe}_{17}$ single crystal measured in magnetic fields of: 1 – 1 kOe; 2 – 2 kOe; 3 – 3 kOe, 4 – 6 kOe, 5 – 9 kOe, 6 – 12 kOe; and curve 7 - $\lambda_{ac}(T)$ for the $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ single crystal measured in magnetic field of 12 kOe.

To obtain information about magnetostriction we investigated the temperature and field dependencies of the longitudinal and transversal magnetostriction for the $\text{Lu}_2\text{Fe}_{17}$ single crystal in the temperature range of 77 – 300 K and magnetic fields (up to 12 kOe) applied parallel and perpendicular to the hexagonal c-axis ([001] direction) [16]. All the curves $\lambda_{cc}(T)$, $\lambda_{aa}(T)$, $\lambda_{ca}(T)$, $\lambda_{ac}(T)$ (the first and second subscripts refer to the directions of the applied field and magnetostrictive strain measurement, respectively) had maxima in the range of transition from the ordered to the magnetically disordered state. The magnetostriction λ_{ac} has the largest value ($\lambda_{\max} = 200 \cdot 10^{-6}$) at $T = 260$ K in magnetic field of 12 kOe (see Fig. 7). As the temperature rises and approaches the magnetic ordering temperature (where the para-process plays the most important role) the magnetostriction deformations significantly increase, approaching their maximum values. The contributions from rotation and displacement of the domain boundaries to magnetostriction of $\text{Lu}_2\text{Fe}_{17}$ are insignificant in the temperature range studied.

In contrast to [16], in low magnetic fields we observed additional features (maxima and minima) on the magnetostriction curves, which correlate well with features found on the $\sigma(T)$ curves which is connected to the complex magnetic structure of the host compound.

Hydrogenation of the $\text{Lu}_2\text{Fe}_{17}$ single crystal leads to a decrease of magnetostrictive deformations (see curve 7, Fig. 7). The experimentally obtained values of magnetostriction for the $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ hydride were three times less than that one in $\text{Lu}_2\text{Fe}_{17}$.

4. Conclusions

The results of hydrogen influence on magnetic and magnetoelastic properties of the $\text{Lu}_2\text{Fe}_{17}$ single crystal can be summarized as follows.

1) Hydrogenation causes the changes of the magnetic state of the $\text{Lu}_2\text{Fe}_{17}$ compound: suppresses the AFM and induces the FM state. An increase of Curie

temperature is observed upon the hydrogen incorporation into the crystal lattice interstices. A change of the magnetic ordering temperature in $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ is connected with the strengthening of exchange interactions in the Fe-sublattice. The ΔT_C values for the $\text{Lu}_2\text{Fe}_{17}\text{H}_{1.5}$ hydride could not be accurately calculated within both the localized and itinerant electrons models.

2) It was found that in low magnetic fields ($H \leq 3.5$ kOe) the temperature dependencies of $\lambda(T)$ and $\Delta l/l$ for the host compound have a set of peculiarities related to the complex magnetic structure of the $\text{Lu}_2\text{Fe}_{17}$ compound. At $H > 3.5$ kOe, the magnetostriction has only one maximum in the range of transition from magnetically ordered to the magnetically disordered state (where the para-process determines the main contribution to magnetization). Hydrogenation of the $\text{Lu}_2\text{Fe}_{17}$ single crystal leads to a decrease of magnetostrictive deformations, as a result of an increase of the magnetoactive ions interspaces. Thermal expansion along the c-axis becomes positive.

Acknowledgements

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THE PROBLEM OF HYDROGEN PERMEATION INTO THE BORON DOPED ELECTRODEPOSITED NICKEL FILMS

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Abstract. This work aim was the researching on the hydrogen penetration into the Ni and Ni-B coatings and on the electrodeposition regimes correlation. The investigations were carried out in the sulfamate nickelling electrolyte with the polyhedral borates class dope. The pH, cathodic current density, electrolyte temperature and alloy boron concentration effects on the hydrogen consumption were studied. The experimental data analysis represented the lower hydrogen consumption in the Ni – B alloy, than in the Ni coating at the same electrolysis regimes.

Keywords: Ni-B, Ni, hydrogen permeation, boron containing dope, pH, cathodic current density, electrolyte temperature

1. Introduction

It is known [1, 2, 3, 4], that the great hydrogen permeation is typical for iron subgroup metals (Fe, Co, Ni), where the hydrogen evolution overvoltage is not large. The feature of the electrolytic coatings thin layers formation by these metals is the significant hydrogen consumption. The growth centers origin on the cathodic foreign material increases the defects number, where the metal-hydrogen interaction is possible. The more the layer thickness is, the homogeneity degree increases and the number of this interactions decreases, so the hydrogen consumption related to the deposit mass is smaller.

The work aim was the researching of the hydrogen penetration into the Ni and Ni-B coatings and electrodeposition regimes correlation. The investigations were carried out in the sulfamate nickelling electrolyte with the polyhedral borates class dope. The electrolysis regimes: $t = 30 - 50$ °C; $pH = 3,5 - 4,5$; $i_k = 0,5 - 4$ A/dm². The hydrogen penetration (V_{H_2} , sm³/ 100 g) into the films was determined with the vacuum extraction method [5, 6].

2. Experimental

V_{H_2} decreases from 260 to 85 cm³/ 100 g for thin Ni films and from 200 to 65 cm³/ 100 g for Ni – B films (related to the 100g coating mass) at the same coating thickness when the cathodic current density (i_k) increases (Fig. 1). This fact is connected both with the lower hydrogen power output (V_{H_2}) (for Ni – B film: $V_{H_2} = 5,39$ % at the $i_k = 0,5$ A/ dm²; $V_{H_2} = 3,74$ % at the $i_k = 4A$ / dm²) and with the smaller coating macro- and microdefects number. For example, the Ni – B film porosity decreases from 25 to 5,7 (pH = 4,0; $t = 40$ °C; boron concentration 0,5 %). The crystal lattice microdistortions number decreases and the mosaic blocks size (D_{HKH}) increases and approaches to the nickel size (for example, nickel D_{HKH} changes from $\sim 3 - 4$ nm at the $i_k = 0,5$ A/ dm² to $\sim 9 - 10$ nm at the $i_k = 4A$ / dm²).

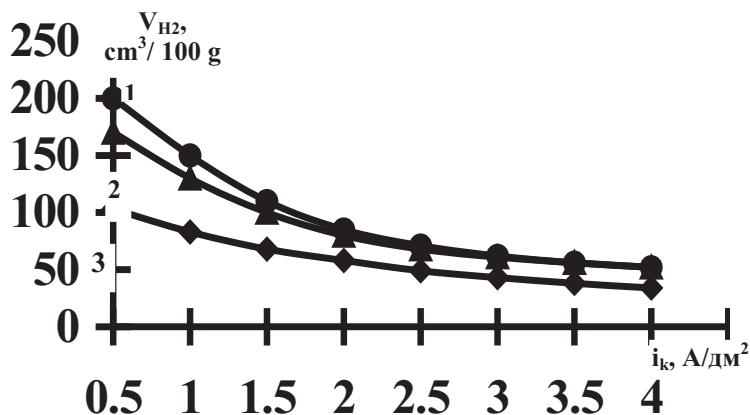


Figure 1. The coatings hydrogen permeation dependence on i_k : 1 – Ni (pH = 4,0; $t = 40^\circ\text{C}$; $d = 4$ mcm); 2 – Ni – B (pH = 4,0; $t = 40^\circ\text{C}$; $C_B = 0,05\text{ g/l}$; $d = 4$ mcm); 3 – Ni – B (pH = 4,0; $t = 40^\circ\text{C}$; $C_B = 0,05\text{ g/l}$; $d = 15$ mcm).

V_{H_2} decreasing from 117 to $88\text{ cm}^3/100\text{ g}$ for nickel coatings and from 90 to $68\text{ cm}^3/100\text{ g}$ for Ni – B coatings with the temperature (t) growth from 30 to 50°C (Fig. 2) is connected with the changes in the nickel and hydrogen interaction conditions. The nickel-hydrogen compounds are characterized by negligible bond energy value ($4,5 \cdot 10^{-20} - 5,8 \cdot 10^{-20}\text{ J}$), so the unstable bonds are destroyed with the temperature increasing, and therefore the evidence of hydrogen inclusion into the deposit is decreased. Besides, the smaller V_{H_2} in the Ni – B film is determined by V_{TH_2} decreasing from 8,48 to 3,84 % (pH = 4,0; $i_k = 2\text{ A/dm}^2$; boron concentration 0,5 %) at the same conditions.

The hydrogen consumption for the Ni and Ni – B coatings thin films grows with the electrolyte acid value (pH) decreasing. For example, $V_{H_2} = 49\text{ cm}^3/100\text{ g}$ at the pH = 3,5 and $V_{H_2} = 88\text{ cm}^3/100\text{ g}$ at the pH = 4,5 for Ni – B (Fig. 3). The crystal lattice microdistortions number and D_{HKH} decrease with pH growth. At the same time the decreasing of the evolving cathodic hydrogen volume leads to the less active crystallization centers blocking, resulting to enhance centers number and to the more equal grained deposit structure; the forming coating becomes less strained. This coating structure changing, obviously, is determined by the so called “nomadic” adsorption $\text{Ni}(\text{OH})_2$ film production on the growing deposit surface, that breaks the normal crystallites growth and leads to the fine dispersed coatings formation. Evidently, H_2 consumption in the coating grows because of the hydroxides inclusion into the deposit at high pH values, in spite of the macrodefects number decreasing (the pores number reducing) and the hydrogen power output (V_{TH_2}) decreasing from 6,34 % at the pH = 3,5 to 4,07 % at the pH = 4,5 ($t = 40^\circ\text{C}$, $i_k = 2\text{ A/dm}^2$; the boron concentration 0,5 %).

It ought to be noted, that the boron containing dope introduction into the nickelling electrolyte causes the noticeable cathodic hydrogen evolution, that is, obviously, connected with the dope dissociation. The evaluating hydrogen is being adsorbed while metal is electrocrystallized, and then is included into the metal coating, leading to its additional hydrogen permeation. The hydrogen permeation degree of the Ni-B coatings increases from 68 to $113\text{ cm}^3/100\text{ g}$ ($i_k = 2\text{ A/dm}^2$; $t = 40^\circ\text{C}$; pH = 4,0) with the boron concentration growth from 0,1 to 1 %, that is represented in the Fig. 4. This dependence is determined by V_{TH_2} changing from

1,96 to 7,05 %, that enlarge the opportunity of the hydrogen inclusion into the coating. The smaller Ni and Ni-B films thickness is, the higher hydrogen permeation degree is. It has been revealed, that the valid alloy boron concentration, when the hydrogen permeation is minimum, is 0,5 %.

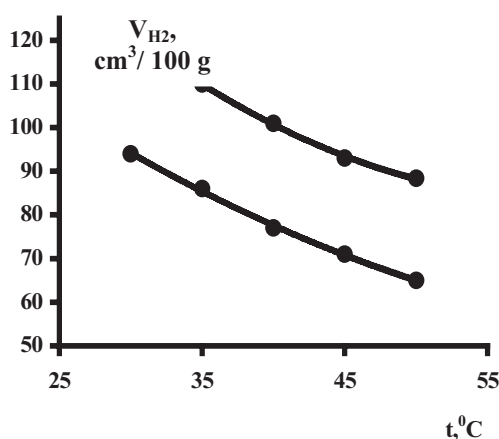


Figure 2. The coatings hydrogen permeation dependence on t: 1 – Ni (pH = 4,0; $i_k = 2$ A/dm²; d = 4 mcm); 2 – Ni – B (pH = 4,0; $i_k = 2$ A/dm²; $C_B = 0,05$ g/l; d = 4 mcm).

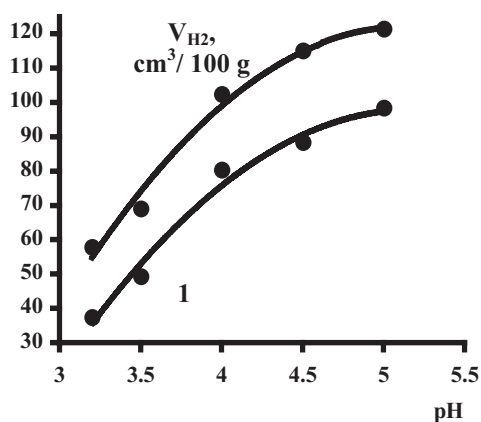


Figure 3. The coatings hydrogen permeation dependence on pH: 1 – Ni ($i_k = 2$ A/dm²; t = 40 °C; d = 4 mcm); 2 – Ni – B ($i_k = 2$ A/dm²; t = 40 °C; $C_B = 0,05$ g/l; d = 4 mcm).

3. Conclusions

The experimental data analysis shows, that the hydrogen consumption in the Ni – B alloy is lower, than in the Ni coating at the same electrolysis regimes. So, when $i_k = 4$ A/dm² for Ni film $V_{H_2} = 85$ cm³/100 g, and for Ni – B - $V_{H_2} = 65$ cm³/100 g, that is 1,3 times smaller. This phenomenon can be explained by the particularities of the Ni – B alloy formation mechanism. When i_k achieves the value higher, than

0,5 A/dm², Ni²⁺ ions discharge into Ni-B⁰ occurs with enhance polarization in comparison with discharge into Ni⁰. The breaking of the Ni²⁺ ions discharge rate, when Ni-B⁰ is electrodeposited (at the $E < -0,75$), is connected with this alloy surface coverage by the adsorbed dope boron containing anions. So, for example, cathodic polarization at the $i_k = 2$ A/ dm² maintained the value 30 mV, and at the $i_k = 4$ A/ dm² - 45 mV.

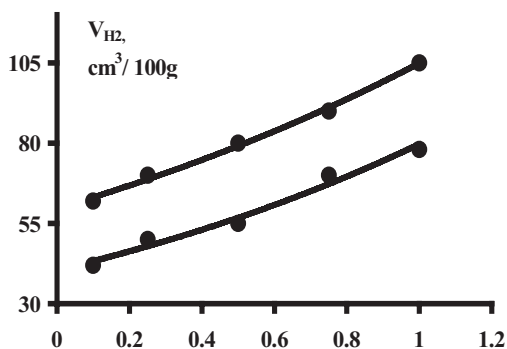


Figure 4. The Ni - B coatings hydrogen permeation dependence on the alloy boron concentration: 1 - d = 4 mcm; 2 - d = 15 mcm. Electrodeposition regimes: pH = 4,0; t = 40° C; $i_k = 2$ A/ dm².

Acknowledgements

The authors are grateful to ICHMS'2005 organizers for giving them the paper representation opportunity.

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HYDROGEN PERMEATION AND NICKEL FILMS STRUCTURE CORRELATION

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Abstract. The present paper aim was the investigation of the electrodeposition regimes influence on the structure and hydrogen permeation of the nickel films under 4 mcm thickness of, received from sulphamate electrolyte. The grain size was calculated and the histograms, characterized the grains distribution with their size, were built according the nickel deposits microstructures photographs. The microtensions values, the mosaic blocks size and the quantitative porosity magnitude were also established.

Keywords: Ni films, hydrogen permeation, microtensions, mosaic blocks, porosity, electrolyte temperature

1. Introduction

The galvanic nickel films of 3 – 8 mcm thickness have found the application in radioelectronic industry and in device-building. The electrochemical nickel coatings receiving method features are the high structural sensitivity and the properties dependence on the electrolyte chemical composition and electrolysis regimes [1, 2, 3]. So, the present paper aim has become the investigation of the electrodeposition regimes influence on the structure and hydrogen permeation of the nickel films under 4 mcm thickness of, received from sulphamate electrolyte [4]. The samples of 500 – 1000 Å thickness on the copper base material were used for the Ni deposits structure detection. The grain size was calculated and the histograms, characterized the grains distribution with their size, were built according the nickel deposits microstructures photographs (increasing in 82000). The microtensions value and the mosaic blocks size were determined by the (111) α и (200) α lines. The quantitative porosity magnitude is represented as porosity surfaces (n) – the pores number, related to the 1 cm² of the galvanic coating [5]. The hydrogen permeation (V_{H_2} , cm³/ 100 g) was determined by the vacuum extraction method. The electrolysis regimes interval: the temperature $t = 30 - 50$ °C; the acidity value pH = 3,5 – 4,5.

2. Experimental

The investigation results are represented in the Figs. 1, 2, 3. The grains distribution with size from their number histogram for the nickel film, received at the $t = 40$ °C, is shown in Fig. 1. We can conclude, that the dominating grains number (68 %) are of the size inside 0 - 400 Å, and the received structure can be attributed to the smallgrained one and the grains shape – to the equalaxial. The electrolyte temperature influence on the nickel films structure is evident from Fig. 1 and Figs. 2, 3 comparison. The electrolyte temperature decreasing to 30 °C leads to the histogram view changing. The maximums shift to the right at the low temperature, and the significant grains dispersion with their size is observed.

The small grains number of 100 – 400 Å diameters is ~ 66 %, the middle of 400 - 800 Å - ~ 40 % and the large with diameter higher than 800 Å - ~ 13 % from the summary grains number. This testifies about nonequalgrained structure formation.

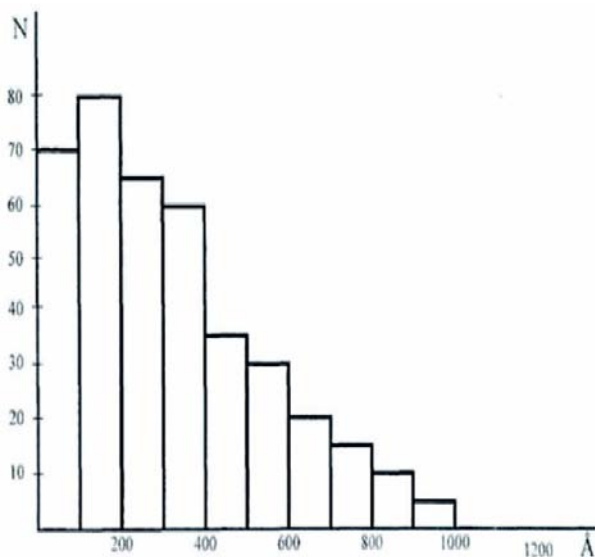


Figure 1. The histogram of the grains distribution with size for nickel film. Electrolysis regimes: $i_k = 2 \text{ A/dm}^2$; $\text{pH} = 4,0$; $t = 40 \text{ }^\circ\text{C}$.

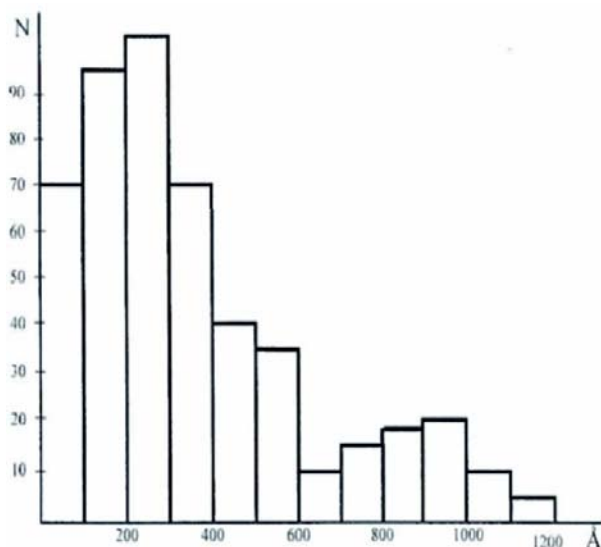


Figure 2. The histogram of the grains distribution with size for nickel film. Electrolysis regimes: $t = 30 \text{ }^\circ\text{C}$; $i_k = 2 \text{ A/dm}^2$; $\text{pH} = 4,0$.

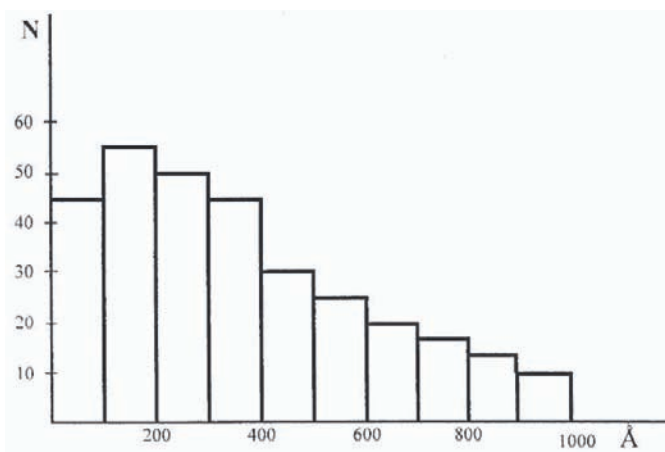


Figure 3. The histogram of the grains distribution with size for nickel film. Electrolysis regimes: $t = 50\text{ }^{\circ}\text{C}$; $i_K = 2\text{ A/dm}^2$; $\text{pH} = 4,0$.

When the electrolyte temperature increases up to $50\text{ }^{\circ}\text{C}$, the grain size is becoming even (Fig. 3). The portion of small grains with size up to 400 Å decreases ($\sim 60\%$), and the grains number with size $800 - 1000\text{ Å}$ increases ($\sim 15\%$). Beginning from the electrolyte temperature $40\text{ }^{\circ}\text{C}$ the large crystallites with size more than 1000 Å disappear (Figs. 1, 3).

The electrolyte temperature influence on the microdistortions and the mosaic blocks dispersion of nickel films is interesting. When t decreases from 40 to $30\text{ }^{\circ}\text{C}$ the microdistortions magnitude and the mosaic blocks size D_{HKL} is becoming smaller. This is connected, evidently, with more intense hydrogen evolution at low temperatures, and numerous pores, unentireties, macrodefects form, because of the simultaneous nickel deposition. Particularly, the pores and defects origin leads to the partial microdistortions relaxation in the coating. The electrolyte temperature increasing from 30 to $40\text{ }^{\circ}\text{C}$ causes the formation of film with less porosity from $17,2$ to $10,4$. The matter is, that at the high nickel sulphamate concentrations $\sim 500\text{ g/l}$, the electrolyte temperature decreasing enhances its viscosity, that makes the molecular hydrogen escape from the deposit surface more difficult, and the coating porosity increases.

It was received, that the largest hydrogen consumption (V_{H_2}) at the $t = 30\text{ }^{\circ}\text{C}$ is $117\text{ cm}^3/100\text{ g}$. The hydrogen consumption variation with temperature in the nickel coating is represented in the Table 1.

TABLE 1. The electrolyte temperature influence on nickel films porosity and hydrogen permeation (coating thickness $d = 4\text{ мкм}$). Electrolysis regimes: $\text{pH} = 4,0$; $i_K = 2\text{ A/dm}^2$

t , $^{\circ}\text{C}$	Porosity n , pores/ cm^2	Hydrogen permeation V_{H_2} , $\text{cm}^3/100\text{ g}$
30	17,2	117
40	10,4	104
50	11,1	88,4

Surface photographs of nickel deposits, received at 30 and 50 °C, are given in Figs. 4, 5.

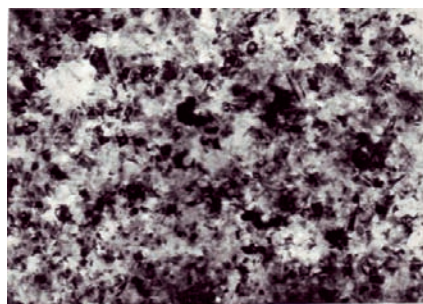


Figure 4. The nickel coating surface, received at 30°C.

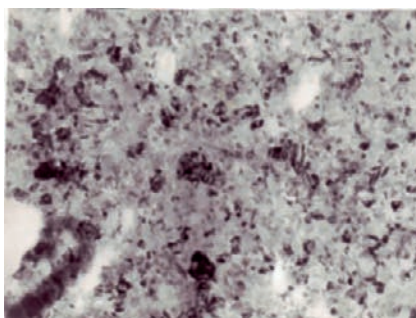


Figure 5. The nickel coating surface, received at 50°C.

3. Conclusions

The coatings, received at the electrodeposition regime: $i_k = 2 \text{ A/dm}^2$, $\text{pH} = 4,0$, $t = 40^\circ\text{C}$, are characterized by less defects and pores number, larger mosaic blocks size, that leads to the microdistortions growth and more tense coating formation. The tensions and D_{HKL} of the coatings, deposited at this regime, are maximal.

The temperature growth from 40 to 50 °C causes the pores number reduction and the hydrogen consumption decreasing in the nickel deposit. At the $t = 50^\circ\text{C}$, $V_{\text{H}_2} = 88,4 \text{ cm}^3 / 100 \text{ g}$. The crystal lattice microdistortions are decreasing when t enhances up to 50 °C. Simultaneously, the lowering of the cathodic evaluating hydrogen quantity leads to the less active crystallization centers blocking, that results in the bigger number of such centers, and the deposit structure is becoming more equalgrained. The coating with less tensions is forming.

The electrolyte temperature growth decreases its viscosity. Thus, the hydrogen desorption from the cathodic surface becomes easy, and the coating porosity decreases.

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The authors are grateful to ICHMS'2005 organizers for giving them the paper representation opportunity.

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INHIBITION OF HYDROGEN PERMEABILITY BY TiN: EVALUATION OF KINETIC PARAMETERS

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Abstract. The thin-film protective coat of titanium nitride (TiN) plotted to stainless steel (brand 12X18H10T) is explored. The mathematical model and methods of parametric identification are described. Kinetic parameters of hydrogen permeability through stainless steel membrane with TiN protective coat are determined.

Keywords: titanium nitride, inhibition of hydrogen permeability, mathematical modeling, kinetic parameters.

1. Introduction

Using hydrogen as fuel is the most perspective direction of the energy development at present. Clean hydrogen does not exist in nature, therefore already existing and (or) new sources of energy are necessary for its production. In particular, the isotopes of hydrogen are used as nuclear fuel in the controlled fusion, which must become the base of energy in future. Interaction of hydrogen with construction materials (CM) (and thus the effect of hydrogen accumulation) stimulates degradation of physical and mechanical characteristics. The solution of this problem is to develop and introduce new hydrogen-resistant materials. If this is impossible, it is necessary to find the ways to protect already existing CM from hydrogen. At present the most justified way of protection from hydrogen corrosion is thin-film coverings.

The influence of titanium nitride (TiN) thin-film coverings to hydrogen permeability of metal membrane was explored in [1]. It was discovered that the coating has good defensive characteristics. It is necessary to understand in detail the mechanism of hydrogen interaction with the covering, to determine the rate constants of these processes, in order to forecast the penetration and accumulation of hydrogen in CM in real use conditions. This work's purpose is to identify the parameters of hydrogen permeability of the defensive covering from titanium nitride (TiN) on stainless steel (brand 12X18H10T).

2. Experiment, model

The high-vacuum plant (the scheme of the vacuum part is in Fig. 1) was used to study hydrogen permeability of titanium nitride. The plant comprise three-stage system of the rollout (roughing-down pump and two ion pump NORD-100, NORD-250), system of hydrogen supply and refinement (the electromagnetic valve V10; the cylinder with unrefined hydrogen; silver-palladium filter F1; the volume

The following model describes hydrogen transfer in metal membrane with the protective coat (stainless steel covered by TiN) for small pressures in the case of the permeability method:

$$\frac{\partial c}{\partial t}(t, x) = D_1 \frac{\partial^2 c}{\partial x^2}(t, x) - a_{11}c(t, x) + a_{12}z(t, x), \quad (1)$$

$$\frac{\partial z}{\partial t}(t, x) = a_{11}c(t, x) - a_{12}z(t, x), \quad (t, x) \in (0, t^*) \times (0, \ell_1), \quad (2)$$

$$c(0, x) = \varphi_1(x), \quad z(0, x) = \psi_1(x), \quad x \in [0, \ell_1], \quad (3)$$

$$\mu s_1 p_0(t) - b_1 c_0^2(t) = -D_1 \frac{\partial c}{\partial x}(t, 0), \quad c_0(t) = c(t, 0), \quad (4)$$

$$D_1 \frac{\partial c}{\partial x}(t, \ell_1) = D_2 \frac{\partial u}{\partial x}(t, 0), \quad (5)$$

$$k_1 c(t, \ell_1) - k_2 u(t, 0) = -D_1 \frac{\partial c}{\partial x}(t, \ell_1), \quad (6)$$

$$\frac{\partial u}{\partial t}(t, x) = D_2 \frac{\partial^2 u}{\partial x^2}(t, x) - a_{21}u(t, x) + a_{22}w(t, x), \quad (7)$$

$$\frac{\partial w}{\partial t}(t, x) = a_{21}u(t, x) - a_{22}w(t, x), \quad (t, x) \in (0, t^*) \times (0, \ell_2), \quad (8)$$

$$u(0, x) = \varphi_2(x), \quad w(0, x) = \psi_2(x), \quad x \in [0, \ell_2], \quad (9)$$

$$\mu s_2 p_{\ell_2}(t) - b_2 u_{\ell_2}^2(t) = D_2 \frac{\partial u}{\partial x}(t, \ell_2), \quad u_{\ell_2}(t) = u(t, \ell_2). \quad (10)$$

Here (1), (2), (7), (8) are the diffusion equations with reversible hydrogen capture by the traps at the membrane layers; (3), (9) are initial conditions; (4), (10) are non-linear boundary conditions of the third kind (Neumann conditions); (5), (6) are mating of layers condition; $c(t, x)$, $u(t, x)$ are concentrations of dissolved atomic hydrogen; $z(t, x)$, $w(t, x)$ are concentrations of hydrogen captured by traps; D_1, D_2 are the diffusion coefficients; μ is the kinetic constant; s_1, s_2 are the shiking probabilities of hydrogen molecules to the surface; b_1, b_2 are the desorption coefficients; $a_{11}, a_{12}, a_{21}, a_{22}$ are the coefficients of hydrogen capture and release by the traps; $p_0(t), p_{\ell_2}(t)$ are for the pressures of molecular hydrogen at input and output sides of the membrane ($\bar{p}_0, \bar{p}_{\ell_2}$ are the constant values of pressures); k_1, k_2 are the rates of hydrogen exchange at the layers joint; ℓ_1, ℓ_2 are the thicknesses of the layers; $J(t) = b_2 u_{\ell_2}^2(t)$ is the output desorption flux density. The hydrogen pressure at the output side is 8-9 orders of value lower than at the input side, therefore we can neglect hydrogen return at the output side: $\mu s_2 p_{\ell_2}(t) \approx 0$.

To describe the hydrogen transfer in material without defensive coat for the concentration pulses method we used the model

$$\frac{\partial u}{\partial t}(t, x) = D \frac{\partial^2 u}{\partial x^2}(t, x) - a_1 u(t, x) + a_2 w(t, x), \quad (11)$$

$$\frac{\partial w}{\partial t}(t, x) = a_1 u(t, x) - a_2 w(t, x), \quad (t, x) \in (0, t^*) \times (0, \ell), \quad (12)$$

$$u(0, x) = \varphi(x), \quad w(0, x) = \psi(x), \quad x \in [0, \ell], \quad (13)$$

$$\mu s p_0(t) - b u_0^2(t) = -D \frac{\partial c}{\partial x}(t, 0), \quad u_0(t) = u(t, 0), \quad (14)$$

$$\mu s p_\ell(t) - b u_\ell^2(t) = D \frac{\partial c}{\partial x}(t, \ell), \quad u_\ell(t) = u(t, \ell). \quad (15)$$

$$u(t, 0) = Q_0 + (-1)^k Q_1, \quad t \in (k\pi/\omega, (k+1)\pi/\omega), \quad (16)$$

$$\bar{u}_0 = Q_0 - Q_1, \quad \bar{u}_0^h = Q_0 + Q_1, \quad Q_0 > Q_1 > 0, \quad \bar{u}_0 = \sqrt{(\mu s \bar{p}_0 - \bar{J})/b}. \quad (17)$$

Here (11), (12) are the diffusion equations with reversible hydrogen capture by the traps; the initial conditions (13); the nonlinear boundary conditions of the third type (14), (15); the expressions (16), (17) describe change of concentration beside surfaces when cracker periodically is turned on and off. Note, that boundary condition (14) is true when cracker is turned off, the last expression in (17) is obtained from (14), (15) when the stationary mode of permeability is reached. The designations of parameters and functions in this model are the same as in model (1)-(10), but without subscripts.

The problem of parameters identification for model (1) - (10) can be divided into two stages. First stage is parameters estimation for samples from stainless steel without defensive covering using model (11) - (17). Then these values are used for identification of the coat (TiN) parameters $D_1, b_1, s_1, a_{11}, a_{12}$ and the parameters of layers joint k_1, k_2 .

3. Parameter identification

The estimation of parameters D, b, s, a_1, a_2 in model (11) - (17) of the hydrogen transfer in stainless steel was made by the identification algorithm based on the Fourier series. The detailed description of the algorithm is in [3, 4]. The experimental data got by the concentration pulses method were used for identification. In addition the estimations of $s, X = Db^{1/2}$ were received by isotherms for the permeability method [3, 4]. Below we describe the identification algorithm based on the Fourier series.

We assume that the time $[0, 2\pi/\omega]$ corresponds to the period of stationary oscillations of the output desorption flux $J(t)$. At the instants of time $t_k = k\pi/\omega$ ($k = 0, 1, 2$) stationary values $\bar{J}, \bar{J}^h$ of the flux $J(t)$ are registered on the half-periods. The cracker is turned off and on correspondingly.

The following expressions connect the unknown parameters of the model (11) - (17) with the measurements (n is the number of harmonic; $\bar{L} = \sqrt{\bar{J}}; \bar{L}^h = \sqrt{\bar{J}^h}$):

$$\begin{aligned} s &= \left[(\bar{J} \ell X^{-1} + \bar{L})^2 + \bar{J} \right] / [\mu \bar{p}_0], \\ \frac{-2J_{<n>} \sinh(\lambda \ell) + \lambda \ell (\bar{J}^h + \bar{J})}{\lambda [2L_{<n>} \cosh(\lambda \ell) - (\bar{L} + \bar{L}^h)]} &= X, \quad n = 0; \\ \frac{-J_{<n>} \sinh(\lambda \ell)}{\lambda L_{<n>} \cosh(\lambda \ell)} &= X, \quad X = \frac{D}{\sqrt{b}}, \quad n = 2m; \\ \frac{n\pi J_{<n>} \sinh(\lambda \ell) + i\lambda \ell (\bar{J}^h - \bar{J})}{\lambda [i(\bar{L} - \bar{L}^h) - n\pi L_{<n>} \cosh(\lambda \ell)]} &= X, \quad n = 2m - 1. \end{aligned} \quad (18)$$

Here:

$$\lambda = \sqrt{\frac{(a_1 + a_2)in\omega - (n\omega)^2}{D(in\omega + a_2)}}, \quad J_{<n>} = \frac{\omega}{2\pi} \int_{t_0}^{t_2} J(\tau) \exp\{-in\omega\tau\} d\tau, \quad L_{<n>} = \frac{\omega}{2\pi} \int_{t_0}^{t_2} L(\tau) \exp\{-in\omega\tau\} d\tau.$$

Let us denote the left-hand side by the fraction $F_1[n, \lambda(n, D, a_1, a_2)]/F_2[n, \lambda(n, D, a_1, a_2)]$. The difference of these fractions must be

zero due to (19)–(21). This allows to use the following object functions for determining D , a_1 , a_2 ($X = \text{Re } F_1 / \text{Re } F_2 = \text{Im } F_1 / \text{Im } F_2$):

$$G_1(n_1, n_2, D, a_1, a_2) = \left| \frac{F_1[n_1, \lambda(n_1, D, a_1, a_2)]}{F_2[n_1, \lambda(n_1, D, a_1, a_2)]} - \frac{F_1[n_2, \lambda(n_2, D, a_1, a_2)]}{F_2[n_2, \lambda(n_2, D, a_1, a_2)]} \right|, \quad (22)$$

$$G_2(n_1, n_2, D, a_1, a_2) = \left[\frac{1}{2} \left(\frac{\text{Re } F_1(n_1, \lambda)}{\text{Re } F_2(n_1, \lambda)} + \frac{\text{Im } F_1(n_1, \lambda)}{\text{Im } F_2(n_1, \lambda)} \right) - \frac{1}{2} \left(\frac{\text{Re } F_1(n_2, \lambda)}{\text{Re } F_2(n_2, \lambda)} + \frac{\text{Im } F_1(n_2, \lambda)}{\text{Im } F_2(n_2, \lambda)} \right) \right]^2. \quad (23)$$

The module of complex value is used in (22). The function (22) serves for rough search in all range of the values D , a_1 , a_2 , while function (23) is used for improving precision of the estimations.

The algorithm of parameter identification is the following.

- 1) Consider the model with no traps, i.e. $a_1 = a_2 = 0$ in equation (11). Estimate D by solving a one-dimensional optimization problem $G_1(n_1, n_2, D, 0, 0) \rightarrow \min$ ($\lambda = \sqrt{i n \omega / D}$). One should choose the harmonics of different evenness, e.g. $n_1 = 3$, $n_2 = 4$. Obtained estimate of D is understated.
- 2) Consider the model with traps, i.e. $a_i \neq 0$. Increase D with small enough increment beginning from the value obtained at the previous step. For each value of D determine a_1 , a_2 by minimizing function (22). Improvement is possible using (23). Optimal values of a_i at the previous step serve as the initial data.
- 3) Calculate the value of X . Determine b using X (better use X obtained from (20) for even harmonic). Obtain s using formula (18).
- 4) Model the desorption flux for the current parameters D, a_1, a_2, b, s and estimate the proximity (for example, in the sense of standard deviation) between the experimental and the model flux. Repeat the steps 2–4 to achieve the best proximity of fluxes with respect to the chosen criterion.

The examples of fitting the experimental fluxes by the model ones for stainless steel are in Fig. 2,3, the results of parameter identification are in table 1,2. These values of parameters were used in the model (1) – (10) instead of parameters $D_2, b_2, s_2, a_{21}, a_{22}$. The identification of parameters $D_1, b_1, s_1, a_{11}, a_{12}$ of defensive coat from TiN and parameters of the layers joint was realized as follows.

1. For the mode of stationary hydrogen permeability (all time derivatives are a zero) from model equations we receive:

$$\begin{aligned} c(t^*, \ell_1) &= (k_2 u(t^*, 0) + \bar{J}) / k_1, \quad u(t^*, 0) = \bar{J} \ell_2 / D_2 + \sqrt{\bar{J} / b_2}, \\ c(t^*, 0) &= \bar{J} \ell_1 / D_1 + c(t^*, \ell_1), \quad c(t^*, 0) = \sqrt{(\mu s_1 \bar{p}_0 - \bar{J})} / b_1. \end{aligned} \quad (24)$$

Let us equate two last expressions and rewrite them for different values of input pressure p_{0i} and corresponding stationary output flux densities $\bar{J}_i$:

$$A_{1i} X_1 + A_{2i} X_2 = B_i, \quad i = \overline{1, n}, \quad (25)$$

$$A_{1i} = \bar{J}_i, \quad A_{2i} = \bar{J}_i \ell_2 / D_2 + \sqrt{\bar{J}_i / b_2}, \quad B_i = \sqrt{\mu s_1 \bar{p}_{0i} - \bar{J}_i}, \quad X_1 = \sqrt{b_1} (\ell_1 / D_1 + 1 / k_1), \quad X_2 = \sqrt{b_1} (k_2 / k_1).$$

This is a system of linear equations for unknown X_1, X_2 , where the right-hand part depends on s_1 . We can get $X_1^1(s_1), X_2^1(s_1)$ choosing a pair of pressures and solving these equations for different values of s_1 . Another pair of $X_1^2(s_1), X_2^2(s_1)$ is received similarly for a second different pair of pressures. Then

$s_1 = \operatorname{argmin}(X_2^1(s_1) - X_2^2(s_1))$. For the known s_1 we determine the values $X_1 = X_1^1(s_1)$, $X_2 = X_2^1(s_1)$.

2. Let us consider the case of high pressure of molecular hydrogen at both sides of the membrane. When some period of time has passed the hydrogen concentration in both layers will become constant and the diffusion flux will vanish; thus we'll have $D_1 c_x(t, \ell_1) = 0$ in the right-hand part of (6). Assuming that for high pressure the concentration is similar to equilibrium we get

$$\frac{k_1}{k_2} = \frac{u(t^*, 0)}{c(t^*, \ell_1)} = \sqrt{\left(\frac{s_2 \mu \bar{p}_0}{b_2}\right) / \left(\frac{s_1 \mu \bar{p}_0}{b_1}\right)} = \sqrt{\frac{s_2 b_1}{b_2 s_1}}.$$

Substituting this to X_2 we get

$$X_2 = \sqrt{b_1(k_2/k_1)} = \sqrt{b_2 s_1 / s_2}. \tag{26}$$

Using (26) we can check the evaluation of the parameters obtained by different methods. Also we can use X_2 from (26) when solving (25) to make the evaluation for X_1 more precise.

3. As TiN is non-metal, $\Gamma_u > \Gamma_c$ (Γ_u, Γ_c are equilibrium solubilities) and thus $u(t, 0)/c(t, \ell_1) = k_1/k_2 > 1$. This inequality and the model equations provide the following estimation for b_1 : $b_1 > (\mu s_1 \bar{p}_0 - \bar{J})/u^2(t, 0)$.

4. Coefficients a_{11}, a_{12} define only flux evolution and don't influence on the stationary flux value. And so we have two limitations $X_1 = \sqrt{b_1}(\ell_1/D_1 + 1/k_1)$, $X_2 = \sqrt{b_1}(k_2/k_1)$ for the parameters D_1, b_1, k_1, k_2 , which determine the stationary flux value. The ratio k_1/k_2 is important when modeling, not k_1, k_2 themselves; thus, choosing k_1 arbitrarily, we get $k_2 = k_1 \sqrt{b_2 s_1 / b_1 s_2} = k_1 X_2 / \sqrt{b_1}$.

5. The simulation of experimental fluxes allows to determine the values of D_1, b_1 . The limitation for X_1 , estimations for the coefficients, and the concentrations inside the membrane layers were taken into account. This considerably restricted the region of parameters. The coefficients $a_{11}, a_{12}, a_{21}, a_{22}$ of hydrogen capture and release by the traps were used to obtain the typical dynamics of reaching the stationary flux level. The kinetic constants were determined using the parameter values for different temperatures.

4. Results and Discussion

Tables 1,2 contain the results of parameter identification of the stainless steel (brand 12X18H10T). Some examples of fitting the experimental fluxes by the model ones are in Figs. 2, 3.

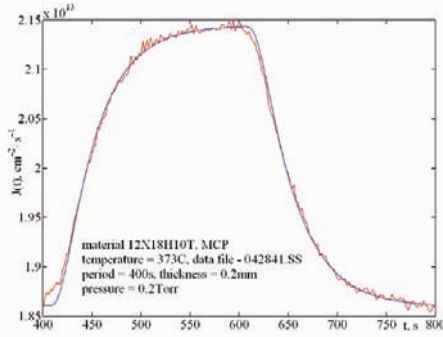
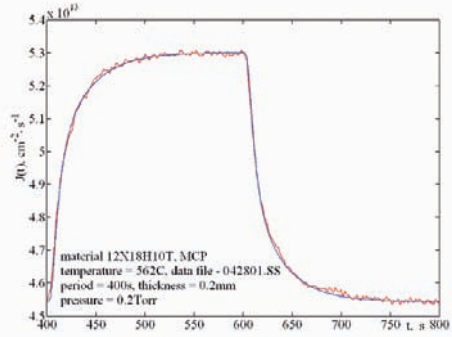
TABLE 1. The identification results of some experimental data for steel (12X18H10T)

$T, \text{ } ^\circ\text{C}$	$D, \text{ cm}^2\text{s}^{-1}$	$a_1, \text{ s}^{-1}$	$a_2, \text{ s}^{-1}$	s	$b, \text{ cm}^4\text{s}^{-1}$	$\bar{c}_0^h, \text{ cm}^{-3}$
370	1.53E-06	0	0	1.85E-06	4.42E-21	4.02E+17
373	1.50E-06	0	0	1.50E-06	4.28E-21	3.56E+17
415	2.28E-06	0	0	2.13E-06	9.84E-21	2.86E+17
431	2.17E-06	0	0	6.14E-06	2.33E-20	3.21E+17
432	2.29E-06	0	0	5.65E-06	2.59E-20	2.89E+17
466	2.68E-06	2.02E-02	4.00E-02	1.37E-05	6.02E-20	2.27E+17

473	4.57E-06	6.84E-02	6.31E-02	1.22E-05	1.83E-19	1.63E+17
522	4.23E-06	3.49E-02	5.54E-02	3.36E-05	2.39E-19	2.37E+17
551	4.93E-06	3.67E-02	5.87E-02	4.88E-05	3.72E-19	2.29E+17
562	4.80E-06	2.86E-02	4.48E-02	5.19E-05	3.78E-19	2.33E+17
596	5.46E-06	3.13E-02	5.57E-02	7.23E-05	4.53E-19	2.45E+17

TABLE 2. Kinetic parameters of stainless steel (brand 12X18H10T)

	D	s	b
preexponential factor	3.09E-04	7.05E-02	5.05E-13
activation energy (kJ/mole)	27.89	59.51	97.14

Figure 2. Fitting of the experimental flux by the model for steel (373°C).Figure 3. Fitting the experimental flux by the model for steel (562°C).

The parameters identification results for the layers of the membrane from stainless steel with TiN protective coat are contained in Tables 3, 4. The approximations of the experimental fluxes by model ones for some temperatures are shown in Figs. 4, 5.

TABLE 3. The identification results of some experimental data for stainless steel (12X18H10T) covered by thin-film from titanium nitride

$T, ^{\circ}\text{C}$	$D_1, \text{cm}^2 \text{s}^{-1}$	$b_1, \text{cm}^4 \text{s}^{-1}$	s_1	a_{11}, s^{-1}	a_{12}, s^{-1}	$D_2, \text{cm}^2 \text{s}^{-1}$	$b_2, \text{cm}^4 \text{s}^{-1}$	s_2	a_{21}, s^{-1}	a_{22}, s^{-1}
380	1.70E-07	3.00E-22	1.39E-10	2.45E-01	1.20E-04	1.81E-06	1.26E-20	1.22E-06	7.00E-03	8.00E-03
420	2.10E-07	4.50E-21	4.15E-10	5.55E-01	4.00E-04	1.70E-06	1.90E-20	2.30E-06	1.10E-02	6.00E-03
460	2.90E-07	4.30E-21	8.77E-10	5.00E-01	7.00E-04	2.30E-06	6.00E-20	4.05E-06	7.30E-02	2.60E-02
500	3.00E-07	2.50E-21	1.71E-09	3.70E-01	2.60E-04	3.50E-06	1.37E-19	6.70E-06	1.60E-01	2.60E-02
565	2.50E-07	3.60E-21	4.44E-09	7.00E-01	1.10E-03	5.63E-06	4.45E-19	1.37E-05	3.00E-01	1.00E-01
585	3.60E-07	2.70E-21	5.78E-09	5.00E-01	1.30E-03	4.20E-06	4.30E-19	1.68E-05	3.30E-02	2.30E-02
600	4.75E-07	3.00E-21	7.00E-09	7.00E-01	2.40E-03	6.60E-06	3.00E-19	2.00E-05	1.30E-01	8.00E-02
615	5.00E-07	2.50E-21	8.39E-09	5.60E-01	1.50E-03	4.20E-06	6.00E-19	2.23E-05	1.60E-01	7.80E-02
$T, ^{\circ}\text{C}$	k_1/k_2	X_2	X_1	$c(t^*, 0), \text{cm}^{-3}$	$c(t^*, \ell_1), \text{cm}^{-3}$	$u(t^*, 0), \text{cm}^{-3}$	$u(t^*, \ell_2), \text{cm}^{-3}$	$\bar{J}, \text{cm}^{-2} \text{s}^{-1}$		
380	1.45E+01	1.20E-12	1.02E-07	2.51E+16	3.92E+15	5.67E+16	1.69E+16	3.60E+12		
420	3.62E+01	1.85E-12	3.20E-07	3.48E+16	2.71E+15	9.80E+16	1.88E+16	6.73E+12		
460	1.82E+01	3.60E-12	2.26E-07	5.39E+16	7.29E+15	1.32E+17	1.50E+16	1.35E+13		
500	8.46E+00	5.91E-12	1.67E-07	1.01E+17	1.84E+16	1.55E+17	1.35E+16	2.48E+13		
565	5.00E+00	1.20E-11	2.40E-07	1.63E+17	2.61E+16	1.30E+17	8.76E+15	3.42E+13		
585	4.27E+00	1.22E-11	1.44E-07	2.07E+17	6.13E+16	2.61E+17	1.11E+16	5.26E+13		
600	5.35E+00	1.02E-11	1.15E-07	2.07E+17	4.63E+16	2.47E+17	1.59E+16	7.62E+13		
615	3.33E+00	1.50E-11	1.00E-07	2.61E+17	1.11E+17	3.68E+17	1.12E+16	7.50E+13		

TABLE 4. Kinetic parameters of TiN and layers joint

	TiN							
	D_1	s_1	b_1	a_{11}	a_{12}			
preexponential factor	1.01E-05	7.45E-04	8.34E-18	5.52	2.29	2.77E-02	2.13E-08	2.85E-09
activation energy (kJ/mole)	22.13	84.12	55.56	15.82	5.29	-37.03	53.45	-26.84

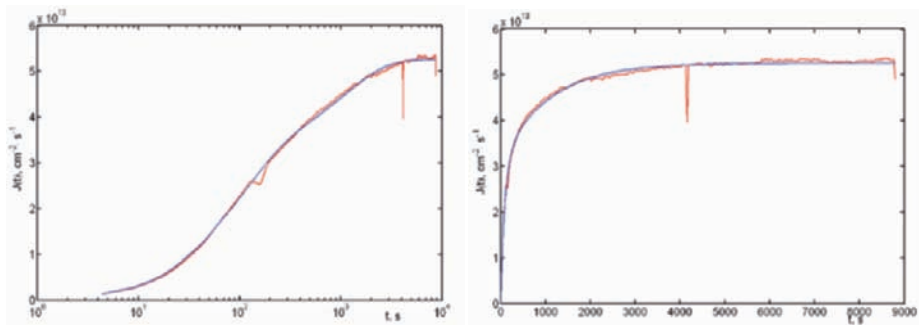


Figure 4. The experimental and model fluxes for steel covered by TiN (585⁰ C).

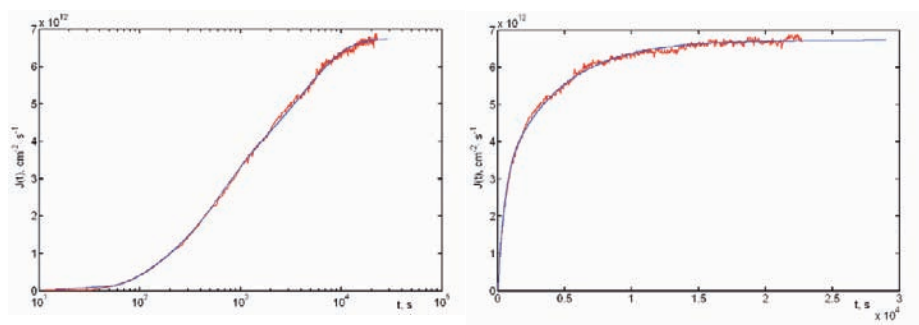


Figure 5. The experimental and model fluxes for steel covered by TiN (420⁰ C).

It is necessary to note that results have some ambiguity as two essential model parameters D_1, b_1 are bound by one restriction, choice of the parameter k_1 is free and there are inevitable inaccuracy of the measurements.

The stationary hydrogen distributions in the membranes from stainless steel without protective coat and with TiN protective coat are shown in Figs. 6, 7 (380⁰ C, 20Torr , other parameters are in the first line of Table 3).

Equilibrium concentrations of diffusive hydrogen for pressure 20Torr are equal to $1.16 \cdot 10^{17}$ and $1.68 \cdot 10^{18}$ for TiN and stainless steel accordingly. Notice that concentration of hydrogen in the near-surface layer of titanium nitride is much less than equilibrium concentration for this pressure. The reason of these phenomena is the small rate of hydrogen adsorption to the titanium nitride surface. Thus hydrogen concentration in stainless steel on border with titanium nitride sharply decreases; this results in the reduction of the penetrating flux and accumulation of hydrogen in steel. The defensive properties of the titanium nitride are determined by its small (compared to metal) adhesion factor of the hydrogen to surface and are explained particularity by its electronic structure.

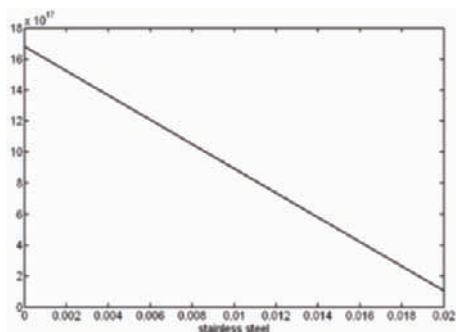


Figure 6. The hydrogen distribution in the steel without TiN coat (380°C , 20Torr).

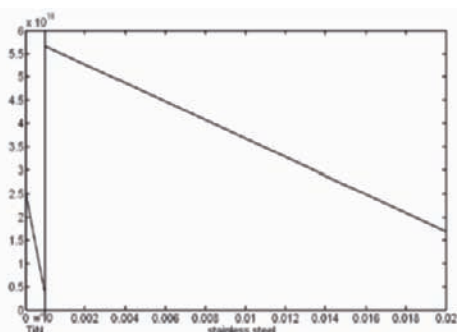


Figure 7. The hydrogen distribution in the steel with TiN coat (380°C , 20Torr).

It is well known that hydrogen adsorption on almost all d-transition metals is exothermal. The hydrogen adsorption on metal of 1B subgroups (Cu, Ag, Au) of the periodic system is connected with overcoming significant activation barrier and comes with energy sorption. These energy costs are bound with the fact that the Fermi level is above the d-zone edge; the density of the electronic states is very low there; this obstructs the dissociation of the hydrogen molecule approaching to the surface and obstructs the determination steady relationship between metal and the

adsorbed atom. It is shown that description of the hydrogen interaction with some non-metal materials can be described by the model earlier offered for the description of hydrogen interaction with metals; one of the main characteristics of solids that define hydrogen adsorption rate on the surface is the density of the conditions at the Fermi level and the free electron concentration.

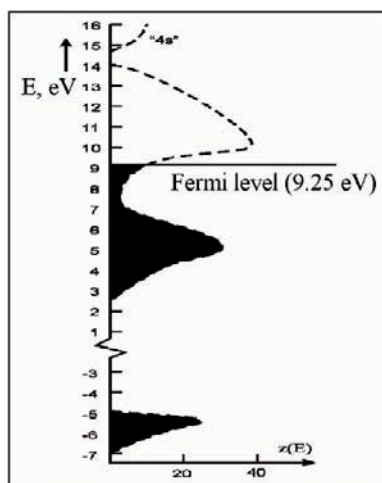


Figure 8. The densities distribution of the electronic states in the TiN.

The studied coats based on titanium have partly semiconductor and partly metallic properties. The concentration of the free carriers is around 10^{19}cm^{-3} i.e. greatly (three orders) less than in metal, but also 3-4 orders more than in semiconductors. The Fermi level in titanium nitride is located in the minimum of the state density formed by intersection of titanium d-zone and p-zone of nitrogen [5] (Fig. 8). Therefore such coats are offered as the most perspective thin-film defensive covering.

5. Conclusions

Studying hydrogen permeability of TiN and mathematical processing of experimental dates allow to determine the kinetic constants of volumetric and surface processes of the hydrogen interaction with the coat. The coefficient of

shaking probability of hydrogen molecules to the TiN is 4 orders of value lower compared to that of stainless steel. This means that adsorption to the surface of TiN is the limiting stage. The low rate of adsorption agrees with the physical conceptions of surface processes and may be explained by peculiar properties of TiN electronic structure. TiN takes place between metals and semi-conductors. The probability of hydrogen molecule to dissociate on the surface of TiN is much less than for stainless steel due to the low concentration of free charge carriers (it is 3 orders of value less at TiN than at metals) and due to the low density of electronic states on the Fermi level.

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DETERMINATION OF HYDROGEN BINDING ENERGY IN VARIOUS MATERIALS BY MEANS OF ABSOLUTE MEASUREMENTS OF ITS CONCENTRATION IN SOLID PROBE

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Abstract. A method for analysis of experimental dynamical curves of high-temperature vacuum-extraction is developed, which allows determining the binding energy and diffusion constants of hydrogen in the probe under study. The experimental data have been obtained using the measuring complex, which allows conducting the absolute measurements of the dynamical curves of high-temperature vacuum- extraction of hydrogen from a solid probe.

Keywords: Hydrogen binding energy, hydrogen analyzer, vacuum extraction, fatigue crack, standards

1. Introduction

The problem of hydrogen storage in metals is related with the problem of determination of hydrogen binding energy and diffusion constants in the metals.

On the other hand, the formation of structure defects (micro cracks, dislocations) in metals and alloys is accompanied by redistribution of concentration of hydrogen diluted in these species.

Hydrogen has very large diffusion mobility; it is accumulated not only in local defects and hydrides but also in zones of stretching mechanical stresses (the Gorski effect [1]).

The increased content of hydrogen in metal serves as an indicator of increased concentration of internal mechanical defects. For this reason, the hydrogen content is controlled in the production of moldings, for instance, the aluminum alloys [3].

Hydrogen influences mechanical properties of construction materials [2]. For example, accumulation of hydrogen inside the metal gives rise to the fact that the material becomes more fragile and easily destroyed. On the contrary, some materials (e.g. titanium alloys) saturated with hydrogen become more plastic, though their ultimate strength decreases.

The natural concentrations of hydrogen in metals are not very high (about 1-10 ppm). Inside the metal hydrogen is located in the traps of different nature (e.g. defects, hydride). The external saturation and mechanical stress leads to changing the picture of the hydrogen distribution between the traps.

Thus, the information about this distribution has the fundamental importance in investigation of the hydrogen – material interactions.

We have developed the high-precision analyzer AV-1 allowing accurate determination of the natural concentrations. The analyzer sensitivity is so high that one can measure the amount of hydrogen in the traps whose volumes are thousands times smaller than the total volume of hydrogen extracted from the probe. On other hand, the AV-1 can be used for the measurements of the high-level hydrogen concentrations (0.1-10 % of mass) in the pieces of material with mass 0.3-0.5 mg.

The high-temperature extraction method with analyzer AV-1 was applied for studying the defect structure of materials undergoing fatigue cracking. In using this method the probe is not heated to the fusion temperature, so that the hydrogen should carry information on the state of the crystal lattice of the metal.

The developed method for analysis of dynamical vacuum-extraction curves allows determination of the binding energy and total volume of the traps of different nature, as well as the diffusion constant of hydrogen in the probe under study.

2. Experimental technique

2.1. HYDROGEN ANALYZER

The high-precision hydrogen analyzer AV-1 is developed for determination of the hydrogen content in metals and alloys in conditions of plant laboratory under exit control of moldings from different alloys. The analyzer works during five years at the metallurgic plants in Kamensk-Uralsk and Samara. The analyzer is included into State list of Measurement Means. The design of apparatus provides very high sensitivity and stability of metrological characteristics. The picture of analyzer is given in Fig. 1.



Figure 1. Hydrogen analyzer AV-1.

The analyzer operation is based on mass-spectrometric principle. The probe preparation system consists of vacuum extractor and oven.

In the process of analysis, a gradual heating of metal probe inside the extractor is made up to the extraction temperature 400-800°C. This temperature is always lower than the fusion temperature of the probe. The gases emitted in the probe heating are analyzed by a mass-spectrometer. Time dependence $q(t)$ of the hydrogen flux is fixed by digital registration system in the form of extraction curve. Such extraction curve for pure aluminum A8 is shown in Fig. 2.

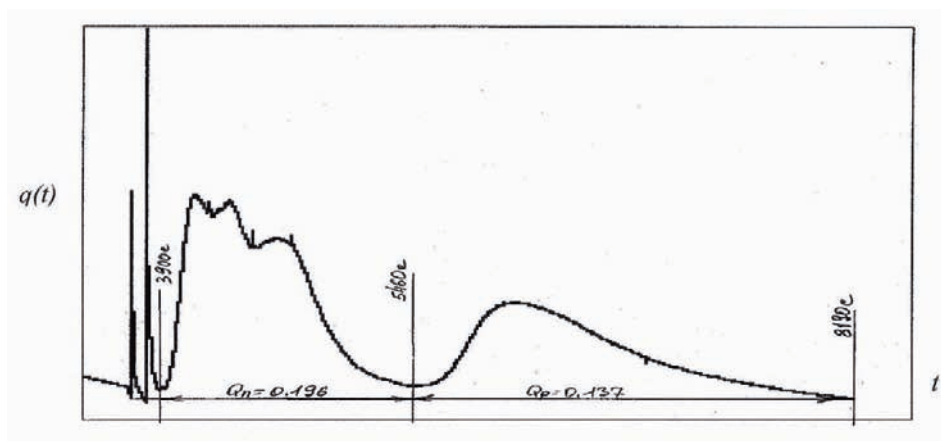


Figure 2. Extraction curve for pure aluminum A8.

2.2. STANDARDS

In determining the hydrogen content in solid probes of titanium, copper and magnesium alloys and in steels, two express-methods are widely used, namely, the spectral method and method of melting in the flux of inert gas carrier. These fast methods require regular (by one shift of even one hour) calibration on the hydrogen content standards – State Standard Probes (SSP). In the SSP passport, the certified concentration of hydrogen in the probe and the allowed deviation with 95% confidence is indicated. For aluminum alloys, the relative value of the allowed deviation varies from 5 to 30%.

When using the absolute methods for determination of the hydrogen content, the probe is heated in vacuum. The gas emitted from the probe is accumulated in a calibration volume. After extraction is finished, the pressure in this volume is measured. From this pressure, the total amount of extracted hydrogen and its content in the probe can be calculated. In such calculations, the hydrogen adsorbed on the probe surface is subtracted from the total amount as a correction known in advance. Such approach can lead to considerable systematic error. The peaks in Fig. 2, corresponding to the surface and diluted hydrogen are separated by vertical lines. The amount of the surface hydrogen Q_n is in 2.4 times larger than that of the diluted hydrogen Q_p .

Figure 3 shows results of determination of the hydrogen content in the SSP of the AMg6 alloy.

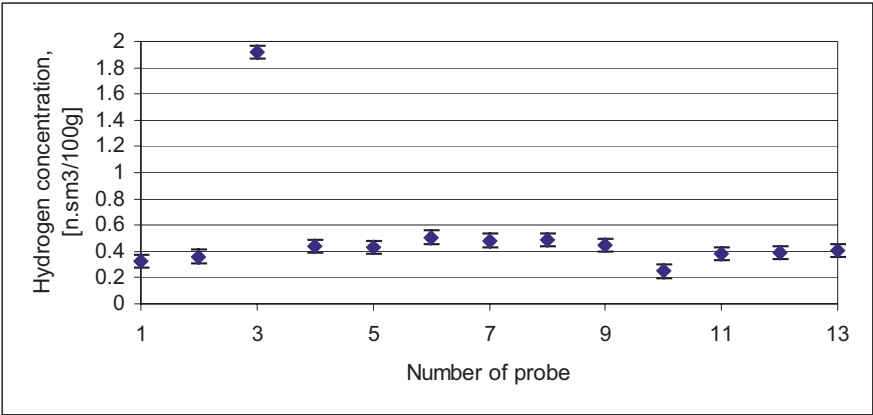


Figure 3. Results of analysis of hydrogen content in SSP of the alloy AMg-6.

The certified value of hydrogen concentration is 0.42 [n.sm³/100g], the certified allowed deviation at 95% confidence is ±0.02 [n.sm³/100g] (error bars at the plot). In presented sample of 13 probes only 46% of results instead of 95% falls into the certified interval, while one probe (8%) has concentration 3.5 times larger, than the certificated one.

It is necessary to note that the calibration is usually made on two probes, so that the probability that one of them will not fall into the certified interval exceeds 0.75, as follows from above experimental data.

In the mass-spectrometric method for hydrogen registration requires calibration of sensitivity of analyzer. The experimental data obtained show that it is necessary to have the standard more stable than the investigated SSP.

We have developed the measure of molecular hydrogen flux in vacuum, for calibration of mass-spectrometer.

Independent testing of the standard was made during 8 months in 2004-2005 at Mendeleyev State Metrology Institute.

The mean value of the hydrogen flux is 7.7·10⁻⁷ m³Pa/s, and the relative value of standard deviation of the accidental component of error of measurements is ±1%. The relative value of allowed deviation at the confidence 90% is 1.7%.

Thus we have the high-precision complex for absolute measurements of hydrogen content in the solid probe of any composition.

3. The study of preliminary stressed probe

3.1. THERMO-MECHANICAL STRESS

Titanium tubes with diameter 22 mm and thickness 2.6 mm were subjected to cyclic non uniform heating for a long time. The temperature difference on the tube length of 15 cm is about 200⁰C. The tube edges were fixed that led to creation of thermo-mechanical tensions. After about 15000 cycles of loading, fatigue cracks were formed at the point with minimum temperature.

The results of determination of hydrogen content in probes cut from various parts of the tube are presented in Table 1.

TABLE 1. Results of analysis of hydrogen content

Probe number	Extraction temperature	Probe mass (mg)	Hydrogen concentration [%] of mass
1	800 ⁰ C	95	0.056
2	800 ⁰ C	90	0.037
3	800 ⁰ C	90	0.021

The scheme of probe position with respect to crack shown in Fig. 4.

The zone of destruction has hydrogen concentration 2.5 times higher than the rest part of the tube.

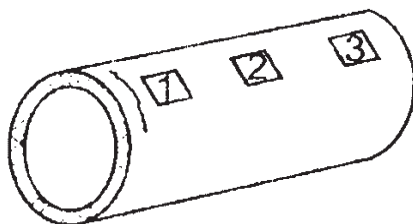


Figure 4. Scheme of probe position with respect to the crack in titanium tube.

3.1. Mechanical stress

The analyzer AV-1 was used for studying aluminum-magnesium alloy with the thickness $h=4\text{mm}$. In cyclic stress, fatigue cracks were formed in the plates. After cutting of the plates in probes with the width 7mm and length 15mm the hydrogen content in the probes were determined. The map of hydrogen distribution with respect to the crack is given in Fig. 5.

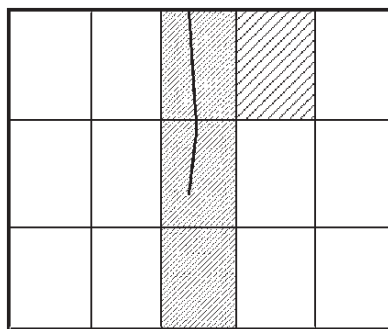


Figure 5. Map of hydrogen distribution in the plate. Thick shading – 2.0 ppm; sparsely shading – 1.7 ppm; in another parts – 1.2-1.3 ppm.

The zone of the line of the formation of the crack has the hydrogen concentration 1.5 times higher than the background concentration. The distance at

which the concentration gradient is observed is about $3h$ (i.e. three plate thicknesses). The increased hydrogen content is observed on the crack line and its continuation where the line is not observed.

4. Estimation of defect density and volume from extraction curve

Suppose that the structure defect has a form of tubes created the joint of three grains, as shown in Fig. 6.

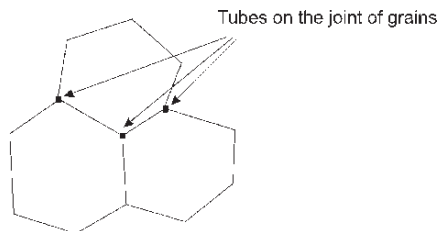


Figure 6. Scheme of the defect position on the joint grains.

According to the data available in literature size of grains in technical pure, not annealed aluminum equals $d=90\mu\text{m}$. Let us take the cavities in the form of tubes. The length of the tube equals the size of the grains. The transverse dimension of the probes not undergoing loading is $\gamma=10\%$ of the length.

To estimate the cavity length, let us suppose that the grain has the form of a cube with length of edge b . Then from the condition of equality of the grain volumes its presentation in the form sphere and cube one obtains:

$$b = \sqrt[3]{\frac{\pi d^3}{6}}$$

In this approximation the volume of one cavity equals $b^3\gamma^2 = 3.8 \cdot 10^{-9} \text{ cm}^3$. The amount of hydrogen at each maximum in Fig. 2 is determined by integration of this maximum and equals $Q_1=1.18 \text{ n.mm}^3$, $Q_2=0.82 \text{ n.mm}^3$, $Q_3=1.8 \text{ n.mm}^3$, $Q_4=2.7 \text{ n.mm}^3$. By dividing the total amount of hydrogen by the volume of single cavity and the volume of the analyzed probe one obtains the concentration of defects corresponding to each maximum: $Z_1=4.2 \cdot 10^5 \text{ cm}^{-3}$, $Z_2=3.2 \cdot 10^5 \text{ cm}^{-3}$, $Z_3= 6.4 \cdot 10^5 \text{ cm}^{-3}$, $Z_4= 9.6 \cdot 10^5 \text{ cm}^{-3}$.

In the above approximation the total number of traps in 1cm^3 of the probe, calculated from hydrogen amount, is $Z=\Sigma Z_i=2.34 \cdot 10^6 \text{ cm}^{-3}$, and the grain concentration is $2.58 \cdot 10^6 \text{ cm}^{-3}$. The concentrations coincide within 10%.

Thus the conclusion can be made that hydrogen at atmospheric pressure fills all cavities along the grain boundaries.

5. Estimation of hydrogen binding energy

The high sensitivity of the analyzer AV-1 and the representative statistics (about 30 thousand points on one curve) allows one to discern some maxima on the extraction curve. The maximum position and shape provides information about the binding energy and total volume of defects for individual peaks (e.g. see Fig. 2).

Let us consider the process of diffusion of hydrogen in aluminum probe in heating in vacuum.

The sample has the form of cylinder (see Fig. 7).

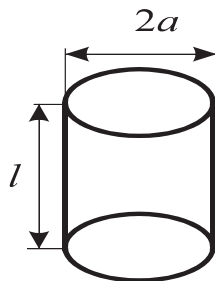


Figure 7. Sample for analysis.

The extractor walls are made of quartz glass their temperature being maintained at constant level T_0 by oven regulator. The quartz has practically zero heat conductivity, the contact between the sample and the extractor walls is pointed, so that the heat transfer occurs via radiation/. The heat flow absorbed by sample is

$$\frac{dQ}{dt} = \sigma S \varepsilon_t (T_0^4 - T^4), \quad (1)$$

were $\sigma = 5,6687 \cdot 10^{-8} \text{ W/m}^2\text{K}^4$ is the Stephan-Boltzmann constant, S is the surface area, T is the sample temperature, ε_t is the absorption coefficient for aluminum, which can be written as,

$$\varepsilon_t = 7 \cdot 10^{-5} \cdot (T + 64,3). \quad (2)$$

The Debye temperature for aluminum is 160°C , so that in the temperature range of interest, $200^\circ\text{--}600^\circ\text{C}$, the heat capacity weakly depends on temperature and equals $C = 1,15 \text{ kJ/kg K}$. The absorbed heat dQ increases the sample temperature by dT ,

$$dQ = C \rho V dT, \quad (3)$$

Were ρ is sample density, V is sample volume.

The use of (1)-(3) leads to the following equation for sample heating:

$$\frac{dT}{dt} = \frac{\sigma S}{C \rho V} \cdot 7 \cdot 10^{-5} \cdot (T + 64,3)(T_0^4 - T^4). \quad (4)$$

The equation for time-dependent hydrogen diffusion in the sample is

$$\begin{aligned} \Delta C &= \frac{1}{D} \frac{\partial C}{\partial t} \\ C|_S &= 0 \\ C|_{t=0} &= C_0 \end{aligned} \quad (5)$$

where C is the hydrogen concentration in the sample, $D = D_0 \cdot \exp(-\frac{u}{kT})$ is the diffusion coefficient of hydrogen in metal, u is activation energy, D_0 is diffusion constant, k and is Boltzmann constant.

Taking in to account cylindrical form of the sample, at given boundary conditions, the first term of Fourier expansion of equation (5) can be written as

$$C(r, z, t) = \frac{C_0 \pi}{0,836} \sin \frac{\pi z}{l} \cdot J_0(\gamma_1 \frac{r}{a}) \cdot f_1(t, u, D_0), \quad (6)$$

where l, a are the cylinder height and radius, respectively, γ_1 is the first root of equation $J_0(\gamma_1) = 0$, $f_1(t, u, D_0)$ is the solution of equation:

$$\begin{aligned} \dot{f}_1 + D_0 \cdot \exp(-\frac{u}{kT}) (\frac{\pi^2}{l^2} + \frac{\gamma_1^2}{a^2}) f_1 &= 0 \\ f_1(0, u, D_0) &= 1 \end{aligned} \quad (7)$$

In performing the analysis, the apparatus registers the total hydrogen flux $q(t)$ through the surface of sample. According to the Fick law, this flux is:

$$q(t) = - \int_S D \frac{dC}{dn} dS, \quad (8)$$

where S is the area of the sample.

Integration of (6) using (8) yields the following expression for the first term of expansion:

$$q(t) = 14,56 \cdot \gamma_1 J_1(\gamma_1) \cdot C_0 \cdot l \cdot \left[\frac{\pi^2 a^2}{2\gamma_1^2 l^2} + 1 \right] \cdot D \cdot f_1(t, u, D_0) \quad (9)$$

When supposing that hydrogen in the probe is contained in traps with different binding energies u_i , and corresponding diffusion constant D_{0i} and hydrogen concentrations C_{0i} , one can use the superposition principle, due to linearity of diffusion equation (5). Then the total flux of hydrogen from the probe $q(t)$ can be expressed by the sum:

$$q(t) = 14,56 \cdot \gamma_1 J_1(\gamma_1) \cdot l \cdot \left[\frac{\pi^2 a^2}{2\gamma_1^2 l^2} + 1 \right] \cdot \sum_i C_{0i} \cdot D_{0i} \cdot f_1(t, u_i, D_{0i}) \quad (10)$$

where $f_1(t, u_i, D_{0i})$ are the solution of equation (7) at given values of the constants u_i, D_{0i}, C_{0i} .

Approximation of the experimental extraction curve by the calculated curve with a proper choice of the initial concentrations C_{0i} and constants u_i, D_{0i} allows one to obtain the activation energy and diffusion constants for hydrogen diluted in the

metal. A plot of the approximating curve for the case of two maxima is shown in Fig. 8.

A plot of the approximating curve for the case of three maxima is shown in Fig. 9.

The experimental curves for the titanium alloy PT-7M is shown on the Fig. 10.

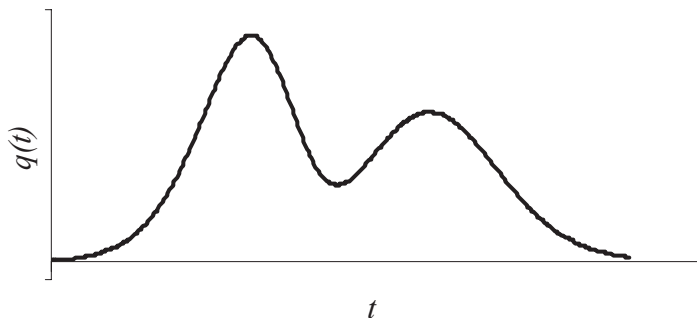


Figure 8. Results of the mathematical modeling for probes of aluminum A8.

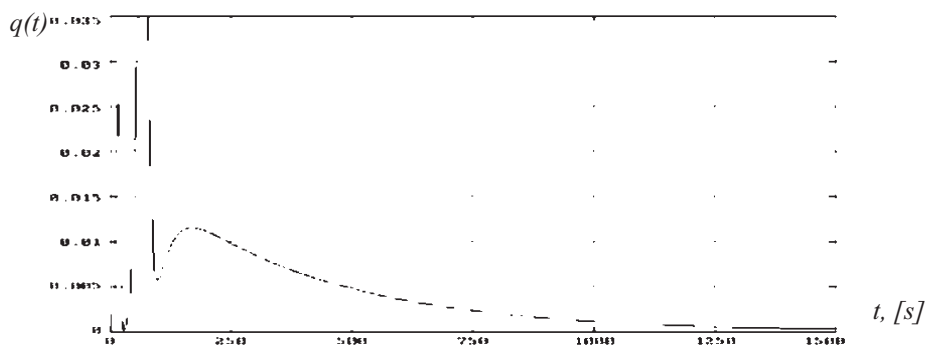


Figure 9. Calculated extraction curve with three maxima.

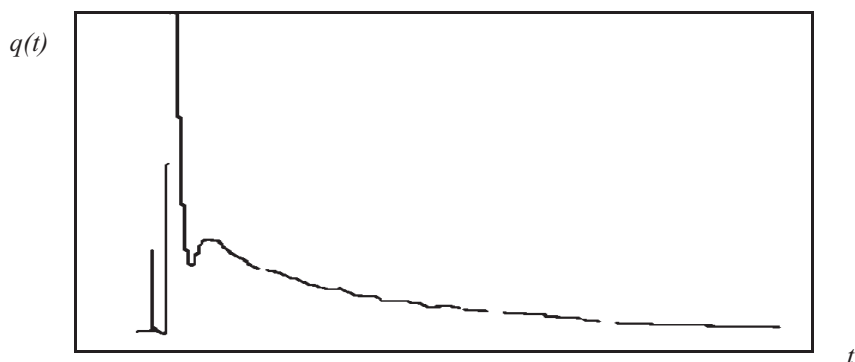


Figure 10. Experimental extraction curve for the titanium alloy PT-7M.

6. Discussion of results

As a result of treatment of experimental extraction curves, the range of activation energies of the traps for aluminum and aluminum alloys was determined. This range stretches from 0.2 eV to 0.8 eV. Consequently, one can suppose that there is no chemically bound hydrogen in the alloys. For the titanium alloys, the maximum activation energy equals 1.5 eV.

The conclusion that hydrogen in technically pure aluminum is concentrated in defects on the edges of grains agrees well with the data of radio graphical investigations. Figure 11. shows the radio graphical picture of aluminum, saturated with tritium [6].



Figure 11. Distribution of tritium on the edges of grains in aluminum. Micro photographical picture [6].

The sharp maxima observed on some extraction curves (e.g. the peaks 1 and 2 in Fig. 12.) correspond to explosive character of hydrogen emission from the traps-defects.

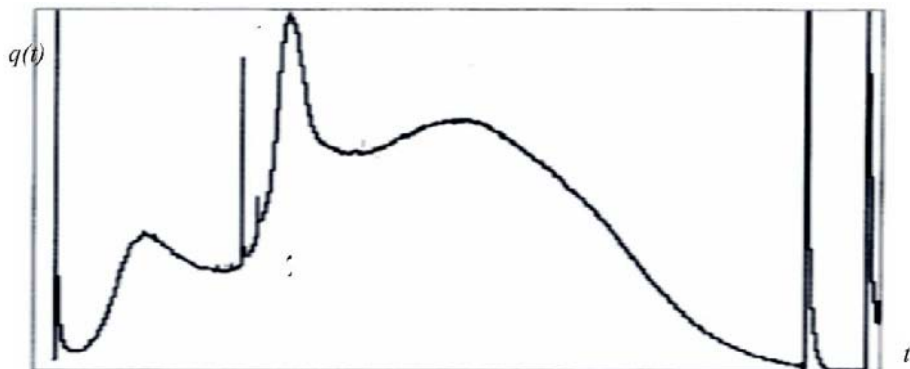


Figure 12. Experimental extraction curve for the aluminum alloy AD-31.

When supposing that hydrogen inside the defects is contained at barometric pressure the volume of defects can be determined from the peak areas. The number of hydrogen molecules corresponding to separate small peaks on the extraction curve is about 10^{11} , that corresponds to the defect volume of about 10^{-6} mm^3 . For aluminum this volume corresponds to the volume of age dislocation.

By comparison, the minimum volume of the defect registered by the methods of ultrasonic inspection is about 0.1 mm^3 that is about four orders of magnitude larger; in the optical microscope, the surface defect with the volume of about 10^{-6} mm^3 can be seen.

The results obtained on the fatigue stress show capability of the suggested method to study surface and bulk structure of metal and, in particular, to estimate the volume of inner fatigue micro-cracks.

Correlation is found between the shape of extraction curve and the type of alloy. Experiments with probes of various shapes and masses show that the number of maxima on the extraction curve does not change.

Unique technical characteristics of method are achieved. The apparatus we developed allow metrological reliable determining the hydrogen concentrations as low as $10^{-5} [\%]$ of mass.

7. Conclusions

Results of our work are as follows:

1. We have developed equipment, which allows obtaining information on the material structure from the hydrogen extraction curve in heating of a probe in vacuum. Accurate determination of the extraction curve provides information both on the hydrogen binding energy in metal and on concentration of spatial micro-traps.

2. It has been established experimentally that fatigue phenomena and destruction of construction materials are accompanied by increasing hydrogen concentration in the destruction zone.

3. Comparison between the results of analysis of the hydrogen content and the data of other authors allows us to conclude that all defects in aluminum are filled with hydrogen at barometric pressure.

4. The proposed calculations procedure allows one to approximate the experimental extraction curve and to determine the diffusion constant and activation energy for each peak of the curve.

5. The values of activation energies obtained from treatment of the experimental data for aluminum and its alloys lie in the range from 0.2 eV to 0.8 eV that allows us to conclude that the chemically bound hydrogen is absent in this alloys.

6. The approach to the study of properties of materials considered above does not require preliminary saturation of the studied probes with hydrogen. Natural hydrogen available in a metal carries information on pre-history of the material that will allow obtaining more complete information from the extraction curves in the further development of the method

7. The metrological complex including the hydrogen analyzer and the calibration standards allows realization of the principle of unity of measurement means in conducting analysis of various metals and alloys and obtaining additional information on the volume and structure of bulk and surface mechanical defects.

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PECULIARITIES OF LOW TEMPERATURE INTERACTION OF MECHANICALLY ACTIVATED TITANIUM HYDRIDE WITH NITROGEN AND OXYGEN

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Abstract. The use of mechanical activation is shown to be efficient for decrease of the temperature of titanium hydride decomposition and its interaction with nitrogen. Intense milling of titanium hydride $\text{TiH}_{1.89}$ results in partial loss of hydrogen and formation of $\text{TiH}_{1.68}$, which in the presence of nitrogen completely transforms into titanium nitride at 500 °C. Under heating in a nitrogen atmosphere, reaction of intramolecular oxidation-reduction takes place at the expense of oxygen absorbed by mechanically activated powder with yielding lower oxide Ti_2O .

Keywords: titanium hydride, mechanical activation, titanium nitride, titanium oxide.

1. Introduction

Lowering of the temperature for interaction of titanium and titanium hydride with nitrogen is promising from the viewpoint of obtaining dispersed refractory nitrides [1] at reduced temperatures. The chemical activity of heterogeneous and solid phase interaction may be raised at the expense of formation of fine defected structure and active surfaces [2, 3]. To intensify the activity of chemical processes with participation of solid substances, mechanical treatment is frequently used. The total energy accumulated by a solid, which is responsible for its reactivity, is connected with rather accumulation of defects in the solid than an increase in the surface area [4]. Nitrogen is known to be an active chemical element in relation to dispersed titanium: in the absence of oxygen, fine-dispersed titanium reacts with nitrogen yet at room temperature. Low temperature decomposition of titanium hydride is one of the ways to obtain active fine-dispersed titanium. Nowadays studying processes of interaction between dispersed titanium hydride or titanium and oxygen or nitrogen is of importance because of lack of necessary data on this problem. As shown in [5], hydrides of the titanium subgroup metals are stable in air at room temperature; however, they react with oxygen at elevated temperatures. The authors of [6] have concluded that titanium hydride $\text{TiH}_{1.54}$ oxidation starts at 773K. It follows hydride decomposition and takes place separately for the metal and the released hydrogen. It is limited by the process of oxygen diffusion through the higher oxide TiO_2 film. Bearing in mind that the energy for hydrogen atom diffusion activation in titanium hydride increases with increasing hydrogen content [7] and that the diffusion rate is proportional to the number of vacant tetrahedrons as well as the fact that the dominant mechanism of hydrogen diffusion in hydride is

diffusion through vacancies, it can be supposed that the temperature of titanium hydride dissociation may be reduced by its intense mechanical treatment.

The aim of this work was to investigate the effect of mechanical activation on lowering of TiH_2 dissociation temperature in a nitrogen atmosphere and the mechanism of interaction of mechanically dispersed hydride with oxygen and nitrogen.

2. Experimental procedure

The titanium hydride $\text{TiH}_{1.89}$ powder with a specific surface area of $0.1 \text{ m}^2/\text{g}$ produced by the Zaporizhzhia titanium-magnesium plant was subjected to intense mechanical treatment in a planetary mill AIR with a rotation speed of 1440 rev/min in a steel drums with steel balls for 15 and 60 min in a nitrogen atmosphere. The latter was created via filling the rolls with liquid nitrogen. To intensify chemical processes and to increase the dispersity and activity of titanium hydride, 5 or 10 mass % urea was added. As-treated powder was heated in nitrogen. The bound nitrogen, oxygen and hydrogen in the initial and final powders were estimated using chemical analysis. The products were analyzed by XRD on a DRON unit in $\text{CuK}\alpha$ radiation. The specific surface area was determined by a thermal desorption of nitrogen. Thermal stability of titanium hydride was determined by differential thermal analysis in an argon flow. The effect of urea addition on the processes of dispersion and oxidation of titanium hydride was studied.

3. Experimental results

The carried-out investigations have shown that in the course of milling in a planetary mill the specific surface area of titanium hydride increases from 0.1 (initial powders) to $7 \text{ m}^2/\text{g}$ for the powders milled for 15 min. An increase in the milling time up to 60 min does not lead to a significant increase in the surface area. The hydrogen content in the initial $\text{TiH}_{1.89}$ was equal to 3.8 mass %. Upon milling for 15 and 60 min it decreased to 3.6 and 3.4 mass %, respectively. As-milled titanium hydride powder was very active: after its discharge the oxygen content increased from 0.1 mass% (in the initial powder) to 3.04 and 3.8 mass % for 15 and 60 min milling, respectively. It should be noted that iron was in-milled to 1 mass % and acted as a catalyst for dehydrogenation of titanium hydride.

Titanium hydride TiH_2 is known to have a cubic fluorite-type structure [6]. Compositions with smaller hydrogen content are characterized by partly non-occupied tetrahedron voids formed by titanium atoms [7]. As seen in the XRD patterns (Fig. 1), the diffraction peaks of titanium hydride milled for 60 min in nitrogen (curve 2) are blurred and shifted towards large angles as compared to those for the initial powder, which points to slight decrease in the crystal lattice parameter. Milling for 15 min involves no diffraction peak shift, though the lines are blurred to the same extent as in the case of milling for 60 min. The line blurring is connected with titanium hydride dispersion: the specific surface area upon intense milling increases by more than an order of magnitude.

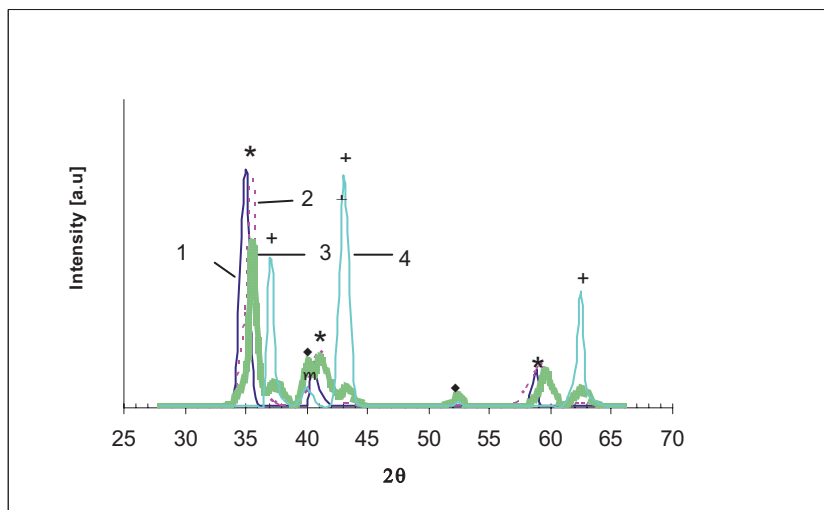


Figure 1. XRD patterns for TiH_2 upon mechanical activation and annealing under a N_2 atmosphere : 1 - initial titanium hydride; 2 - upon mechanical activation for 1 h; 3,4 - upon mechanical activation and annealing at 300°C and 500°C , respectively. (*)- TiH_2 ; (+)- TiN ; (♦)- Ti_2O .

The shift of diffraction peaks towards large angles is an evidence to decrease in the crystal lattice parameter. The interplane distance in the milled for 60 min titanium hydride reduces from 2.57 to 2.54 Å, which corresponds to a change in the crystal lattice parameter of titanium hydride from 0.45 to 0.440 nm. Our results are in good agreement with the data of [6], which have shown that compositions of titanium hydride with smaller hydrogen content are characterized by a defected structure with partly non-occupied tetrahedron voids in a face-centered cubic sublattice of titanium atoms. This effect is quite natural since with dehydrogenization the atom-atom distance decreases and thus the crystal lattice parameter decreases as well. Forming after hydrogen removal defective structure inclined to absorption of air oxygen with initial hydride structure remaining.

The DTA data confirm the fact of partial TiH_2 decomposition and absorption of oxygen under its discharge. Comparison of the DTA hydrogen desorption curves for the commercial initial titanium hydride and that milled for 60 min in a hydrogen atmosphere is shown on Fig. 2. In the initial titanium hydride an endothermic effect is observed above 500°C and equals 120 kJ/mol, which is consistent with data [6]. Milling in a hydrogen atmosphere leads to marked decrease (by 150°C) in the temperature of hydrogen desorption start and to slight decrease in the temperature of decomposition. For titanium hydride milled for 15 min or 1 h in a nitrogen atmosphere, an endothermic effect of dehydrogenization is absent. This effect may be attributed to simultaneity of endo- and exothermic processes which take place in activated titanium hydride under heating in argon. From the data of the chemical analysis, the hydrogen content upon mechanical treatment in a planetary mill is equal to 3.4 mass%, which corresponds to the

formula $\text{TiH}_{1.68}$. The width of titanium hydride homogeneity region (from TiH_2 to $\text{TiH}_{1.5}$) is big and depends on temperature and pressure. The enthalpy of hydride formation depends on its composition and changes from 14.2 for $\text{TiH}_{1.61}$ to 121.3 kJ/mol for $\text{TiH}_{1.97}$ [6]. Therefore, a marked decrease in the endothermic signal for the composition $\text{TiH}_{1.68}$ upon milling in a planetary mill is quite expected.

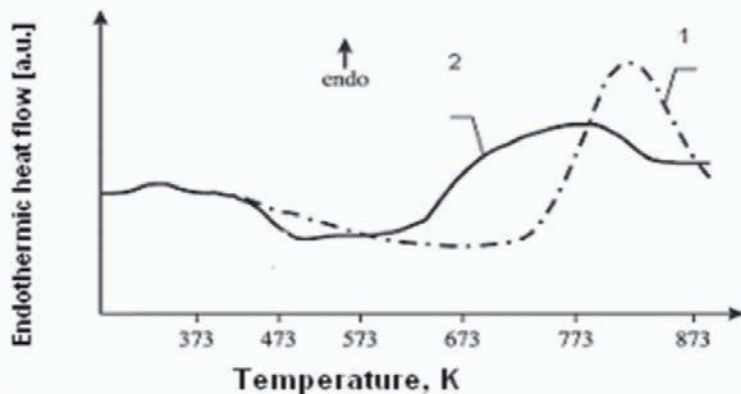


Figure 2. Thermograph of $\text{TiH}_{1.89}$ dehydrogenization: 1- initial, 2- upon mechanical treatment in a hydrogen atmosphere.

Judging by the chemical analysis results on oxygen content, titanium hydride milled for 60 min absorbs to 3.8 mass % oxygen with the hydride structure remaining. Under heating in argon, reactions of intramolecular oxidation-reduction of titanium, accompanied with an exothermic effect, proceed. The absence of any thermal effect on the DTA curve for titanium hydride milled in a nitrogen atmosphere may be related to annihilation of the endothermic signal obtained for titanium hydride decomposition and the exothermic signal corresponding to oxidation processes in the course of heating of active oxygen-containing powder.

Milling of titanium hydride admixed with 15 mass % urea for 60 min in a nitrogen atmosphere results in the formation of titanium oxides during the milling (Fig. 3) represents XRD patterns for hydride powder milled with urea addition. As seen (curve 2), upon milling this powder, the formation of oxide titanium phases is observed and the titanium oxide phase TiO_{2-x} precipitates; shift of titanium hydride diffraction peak (220) being absent. The XRD pattern for titanium hydride powder milled for 60 min with 5 mass % urea additions is identical to that for powder milled without urea (curve 2, Fig. 1): the lines are blurred and slightly shifted towards larger angles.

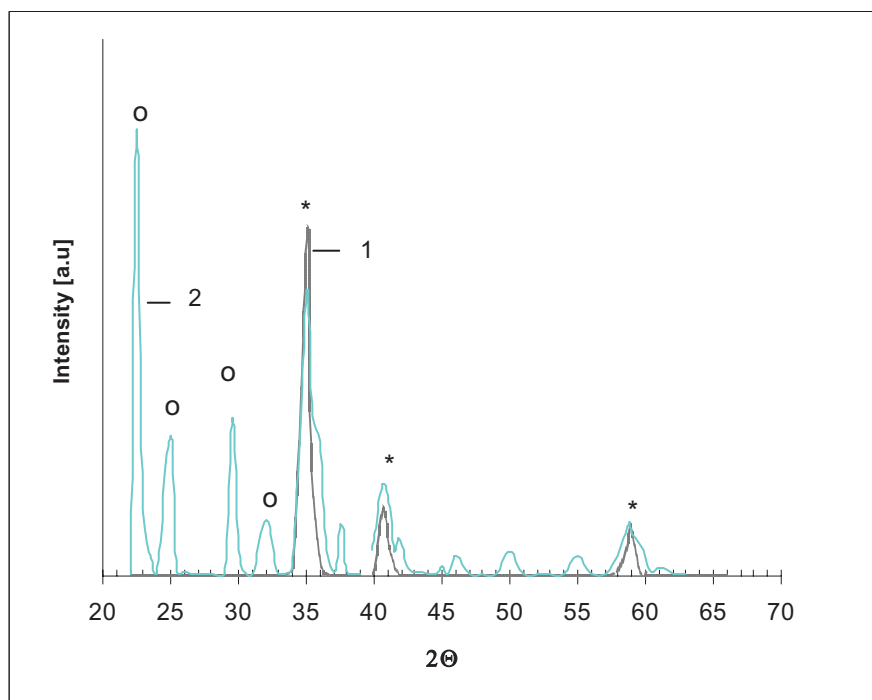


Figure 3. XRD patterns for TiH_2 :

1 -initial titanium hydride; 2 - titanium hydride with additions of urea milled for 1 h

(*) – TiH_2 ; (o) – TiO_{2-x} ;

Nitration processes in dispersed titanium nitride were studied in flowing nitrogen for 1 h at 300, 400, 500 and 600 °C. The phases formed at 300 °C are shown in Fig. 1 (curve 3). As seen, at this temperature partly decomposed titanium nitride oxidizes with the formation of Ti_2O . On the other hand, nitration processes start through stages of titanium nitride decomposition, which is confirmed by decrease in the titanium hydride peak and formation of titanium nitride TiN , that is, above 300°C titanium hydride in a nitrogen atmosphere transforms into titanium nitride. At 400°C titanium hydride decomposition proceeds with a high rate and the intensities of TiN lines increase. However, at a holding of 1 h at 400 °C in a nitrogen atmosphere the titanium hydride phase is still observed, and only temperature rise to 500 °C causes the disappearance of the TiH_2 phase and formation of titanium nitride (Fig. 1, curve 4). It should be noted that the powder milled for 60 min is more active compared to titanium hydride milled for 15 min: upon heating titanium hydride powder activated for 15 min, at 500 °C the diffraction peaks corresponding too titanium hydride still remain. In the course of heating titanium hydride admixed with 15 mass % urea in a nitrogen atmosphere, the oxide phase TiO_{2-x} formed during powder milling transforms into the phase Ti_2O . It may be supposed that processes of higher oxides reduction take place at the

expense of the urea $\text{Co}+\text{NH}_3$ decomposition products and the hydrogen released due to titanium hydride decomposition. As established in [8], under heating titanium dioxide reduces by hydrogen to lower oxides. It is worth noting that at 600 °C the lowest content of the oxide phase Ti_2O is in powder with 5 mass % urea.

4. Conclusions

1. It has been established that under intense milling in a planetary mill in a nitrogen atmosphere, titanium hydride may decompose with formation of defected structure characterized by partly non-occupied tetrahedron voids in a face-centered cubic sublattice of titanium atoms. This effect is accompanied by decrease in the crystal lattice parameter of titanium hydride subjected to intense milling for 60 min.
2. Formation of the above structure promotes intense absorption of air oxygen by the surface of dispersed titanium hydride.
3. The fact of intramolecular oxidation-reduction of dispersed titanium hydride powder under heating above 300 °C in a nitrogen atmosphere at the expense of adsorbed oxygen has been established.
4. Intense milling has been shown to cause a decrease in the titanium hydride decomposition temperature.
5. Processes of nitration of titanium hydride are shifted towards low temperatures.

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METAL HYDRIDE USE FOR SOLAR ENERGY ACCUMULATION

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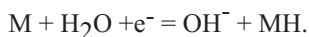
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Abstract. In the present work it is for the first time proposed to use a photoelectrochemical cell with a GaAs photoanode and a metal hydride cathode based on intermetallic alloys $\text{LaNi}_{5-x}\text{Co}_x$, where $0 \leq x \leq 2.5$ for solar-to-hydrogen conversion with possibility to storage hydrogen in a cathode material. The characteristics of photoanode and cathodes have been investigated and results obtained are discussed.

Keywords: solar-to-hydrogen conversion, photoanode, metal hydride, kinetic characteristics, equilibrium potential

1. Introduction

The solar-to-hydrogen conversion by the photoelectrochemical method of water splitting is one of prospective methods for solar energy accumulation. A conventional photoelectrochemical cell for water splitting consists of semiconductor photoanode and a metal, usually Pt, cathode immersed in the aqueous solution of electrolyte and separated by cation-exchange membrane [1]. Oxygen is released at the photoanode and hydrogen – at the cathode under illumination of the photoanode by sunlight. The cathode reaction may be changed by hydrogen storage reaction in the metal hydride (MH) material of cathode:



It also permits storage hydrogen at suitable technological form. Such a cell has been described in literature now [2]. Photoanode based on SrTiO_3 with bandgap $E_g = 3.2$ eV was used in work [2]. Such choice provides energy sufficient for water splitting (1.23 eV) and for overcoming losses related with electrode overpotential. But the efficiency of solar-to-hydrogen conversion is low in this case because only the small UV part of sunlight spectrum with $h\nu > E_g$ takes part in the reaction generating cross-bandgap transitions. In our work it has been for the first time demonstrated possibility to charge MH by narrow bandgap photoanode, in particular GaAs (Fig. 3b).

This semiconductor has the optimum bandgap for sunlight conversion (1.42 eV) and so, like Si, is commonly used for solid-state photovoltaic elements. In our case the complete water decomposition for hydrogen and oxygen does not take place.

The products of anode- and cathode reaction - sulphide ions and hydroxyl ions respectively are accumulated in their half-cells and induced concentrative electromotive force hindering MH charging. However, MH charging reaction is possible. We also tried to determine MH materials that are the most appropriate for this application.

2. Experimental details

The intermetallics $\text{LaNi}_{5-x}\text{Co}_x$, where $0 \leq x \leq 2.5$, were selected for investigation as cathodes. Such cathodes possess high cyclic stability that permits use them successfully for Ni-metal-hydride batteries [3]. The work consists of three parts: calorimetric, electrochemical and photoelectrochemical investigations. The integral enthalpy of hydrogen desorption was determined in calorimetric experiments at calorimeter modernized IT-s-400. The powders of alloys were previously saturated by gaseous hydrogen. The samples for electrochemical investigations were prepared by pressing powders of the above mentioned alloys mixed with the aqueous solution of carbon fluoride (~ 4 wt.%) on Ni net at a pressure of 125 kg/cm^2 . The cathodes (0.2 g) were prepared in the form of tablets with 8 mm diameter and 1mm width. Two-stage activation was carried out before measurements: samples were boiled in 6M KOH during 1.5 h and then they were electrochemically cycled (4 cycles) from -0.5 V to -1.2 V . All potentials in the work are vs. Hg/HgO electrode. The measurements were performed with a potentiostat P5848 in the three-electrodes cell with Pt counter electrode and Hg/HgO/6M KOH reference electrode under room temperature. Equilibrium potential, $E_{\text{MH/M}}$ was determined from charging curves by interrupting current under the different degree of saturation on plate [3]. Discharge capacity, C_{dis} was calculated from discharge curves after reaching electrode potential -0.6 V . The electrodes were charged by current 100 mA/g during 3 h and discharged by current 50 mA/g . Quasi-stationary I-V cathode curves were measured under stepwise varying potential with the rate of 10 mV/2 min .

A single-crystal GaAs was used as the photoanode for the photoelectrochemical experiments. The measurements were carried out in the cell with quartz window. Cathode's and anode's areas of the cell were separated by an ion-exchange membrane. The photoanode was placed in polysulphide electrolyte: $1 \text{ mol/l Na}_2\text{S} + 1 \text{ mol/l S} + 1 \text{ mol/l NaOH}$ and cathode in 30 % KOH solution. The spectral characteristics of photoelectrochemical current were measured at experimental setup described in the work [4]. The accumulation of hydrogen was investigated under radiation flux 75 mW/cm^2 . The surface of GaAs was modified by Pt nanoparticles by the method of electrodeposition under strong illumination of the semiconductor. The Pt films on GaAs surface were investigated with Auger electron spectrometer JAMP-10S and with transmission electron microscope (TEM) EM-200 under accelerating voltage 100 kV .

3. Results and Discussion

3.1. ELECTROCHEMICAL INVESTIGATIONS

THE RESULTS OF ELECTROCHEMICAL MEASUREMENTS ARE REPRESENTED IN TABLE 1

TABLE 1. The results of calorimetric and electrochemical investigations

Materials	H _{des.} kJ/mol H ₂	E _M , act V	E _{MH/M} V	I _o , mA	b*, V	a*, V
LaNi ₅	31.6	-0.82	-0.934	0.10	0.06	0.14
LaNi _{3.5} Co _{1.5}	32.7	-0.80	-0.93	0.10	0.07	0.13
LaNi ₃ Co ₂	36.0	-0.88	-0.928	1.0/4.5**	0.06/0.12	0.055
LaNi _{2.5} Co _{2.5}	37.3	-0.89	-0.926	3.0/8.9	0.06/0.12	0.030

*a, b – const. in the Tafel equation; a given under i = -10 mA.

** - the values of Tafel slopes, the numerator – the first section of the curve, the denominator – the second section of the curve (Fig. 1b).

As shown in Table 1, there is the cathode shift of equilibrium potential for activated but uncharged electrodes E_{M,act} with increasing Co content. But the equilibrium potential of charged electrodes, E_{MH/M} was varied very slightly, about 10 mV. This is in agreement with the result of work [5] where the slight varying of equilibrium hydrogen pressure at plate for these materials under varying Co content was shown. The discharge capacity for first cycle increased with a rise of Co content. The kinetic investigation of cathode process demonstrated increasing the catalytic activity of the surface for hydrogen releasing reaction under substitution Ni for Co. The significant acceleration of cathode process simultaneously with decreasing overpotential η especially for $x \geq 2$ was observed in this case (Fig. 1).

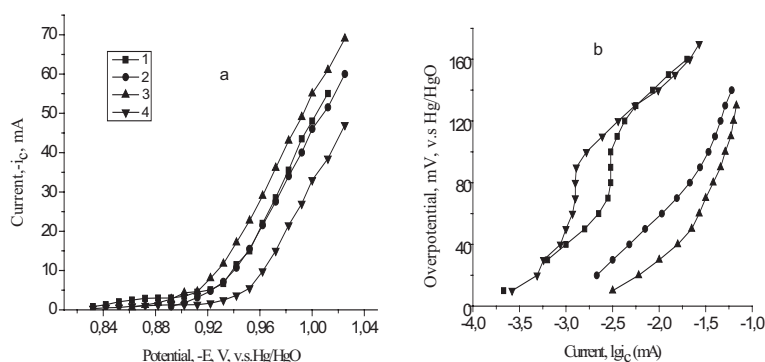


Figure 1. The cathode current-voltage curves for LaNi_{5-x}Co_x electrodes. The x values: 1 – 1.5, 2 – 2.0, 3 – 2.5, 4 – 0.

The view of relationship $\eta(\lg I_k)$ was changed with varying Co content in the alloys. The curves for LaNi_5 and for alloys with $x \leq 1.5$ were identical and were characterized by the section of the curve with limiting current under low overpotential and the linear section of the curve with slope $RT/F = 0.06$ V under high overpotential. The curves with $x \geq 2$ were characterized by the two linear sections with slopes 0.06 and 0.12 V. It has been known that hydrogen releasing reaction goes according Volmer-Tafel mechanism for LaNi_5 during which the process is limited by the stage of the slowed down recombination of absorbed hydrogen atoms (Tafel reaction) [6]. The analysis of data obtained permits suppose the same mechanism for our alloys. But the limiting stage of process is changed for $x \geq 2$ under negative shift of potential and discharge (Volmer reaction) becomes limiting.

Exchange currents, I_0 (Tab. 1) were obtained by extrapolation of the linear segments of $\eta(\lg I_k)$ functions to $\eta = 0$. This current increased with increasing Co content and for $x \geq 2$ exceeded the corresponding value for LaNi_5 more then one order of magnitude.

So the introduction of $2 \div 2.5$ Co atoms into LaNi_5 made cathode hydrogen releasing much easier, namely, the process is accelerated and goes under lower overpotential.

3.2. CALORIMETRIC INVESTIGATIONS

The thermograms of hydrogen desorption from MH is represented on Fig. 2.

The thermograms with Co content $x < 1.5$ are characterized by one maximum about 375 K. The shift of this maximum to higher temperature and appearing furthers maximums at higher and lower temperature is observed with the rise of

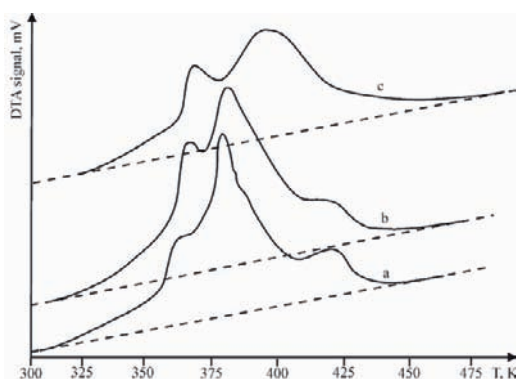


Figure 2. The thermograms of hydrogen desorption: a - $\text{LaNi}_{3.5}\text{Co}_{1.5}\text{H}_{6.77}$; b - $\text{LaNi}_{3.0}\text{Co}_{2.0}\text{H}_{6.68}$; c - $\text{LaNi}_{2.5}\text{Co}_{2.5}\text{H}_{6.55}$.

Co content. The integral enthalpy of desorption, H_{des} was calculated from these data (Table 1). As seen from Table 1, the enthalpy grows with increasing Co content. That is, substitution Ni atoms for Co in amounts of more than two atoms results in the formation of several forms of bonded hydrogen with the different strength of bonds. The increasing strength of bonds in hydronized $LaNi_{2.5}Co_{2.5}$ is evidently the reason of decreasing equilibrium hydrogen pressure as compared with $LaNi_5$.

3.3. PHOTOELECTROCHEMICAL INVESTIGATIONS

The photopotential of GaAs electrode, E_f has to be about -1.0 V for effective MH charging (see Table 1, $E_{M/MH}$). At the same time E_f had value -0.7÷-0.8 V. The E_f increased of 0.25÷0.3 V after Pt nanoparticles deposition on GaAs surface that leads to near optimum charge regime. The presence of Pt on GaAs surface was confirmed by Auger spectroscopy method (Fig. 3).

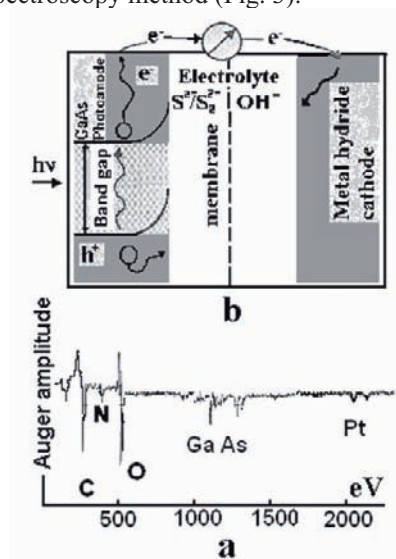


Figure 3. The scheme of photoelectrochemical cell for hydrogen storage (a) and Auger-spectrum of GaAs surface modified by Pt (b).

As seen in Fig. 3a, impurities on the surface (C, N, O) accompanies Pt deposition. The value of inter-planes distance for {200}, $d = 0.203$ nm was established under investigations of Pt films with TEM. Thus the lattice constant for Pt on GaAs surface is: $a = 2d = 0.406$ nm. This value is higher as compared with that given in literature, 0.392 nm [7]. The larger value in our case may be explained by impurities likely implanted in the Pt lattice or by the interaction of Pt with GaAs surface. The Pt particles with average dimension $5 \div 10$ nm were obtained with our technique [8].

The efficiency of solar-to-current conversion was $10 \div 12$ % for pure GaAs electrodes and $12 \div 16$ % for modified by Pt. The spectra of quantum yield of photoelectrochemical current, η_i were investigated to establish the reason of the

increasing efficiency (Fig. 4). The rising of η_i with increasing anode potential and after Pt modification was established. The current-potential theoretical relationship (1), was used for the analysis of the data obtained [9]:

$$I = \frac{Pek_s^a}{s_p(E) + k_s^a} - i_0 \left(1 + \frac{\Delta n_1}{n_0}\right) \exp[-e(\Delta E_{sc} - \alpha \Delta E_H)/kT], \quad (1)$$

were I – total current; P – light intensity; k_s^a – the anode reaction constant; $s_p(E)$ – the rate of surface recombination for minority carriers (holes for n-GaAs); i_0 – exchange current for majority carriers, electrons; α – the transport coefficient for this reaction; ΔE_H – the fall of potential in double ion layer; n_0 – electron concentration in the conductive band of GaAs; Δn_1 – the growth of concentration on the boundary of space charge region (SCR) with quasi-neutral volume; ΔE_{sc} – the fall of potential in SCR.

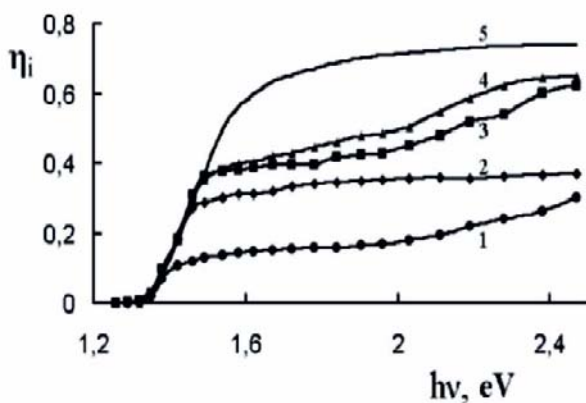


Figure 4. The quantum yield of photoelectrochemical current as the function of quantum energy of light beam for initial GaAs electrode (1, 3) and for modified by Pt (2, 4). Potentials, E: 1, 2 – -0.5 V; 3, 4 – -0.1 B. 5 - theoretical curve for $E = -0.1$ V, $s_p = 0$.

The left part of equation (1) describes hole photocurrent and the right part – electron cathode current. The variation of ΔE_H did not exceed 50 mV under potentials from $+0.6$ to -0.5 V as it was established from Mott–Schottky plots [10]. Using known parameters for semiconductor (diffusion coefficient and diffusion length for electrons and holes) and values for $k_s^a = 2.6 \cdot 10^3$ cm/s and $i_0 = 10^{-6}$ A/cm² obtained by us for GaAs in polysulphide electrolyte it was established that decreasing I with increasing cathode potential is mainly caused by the rise of the velocity of surface recombination under $E \leq -0.1$ V (Fig. 4). Theoretical relationship $\eta_i(h\nu)$ was calculated similarly to [9] under potential $E = -0.1$ V (curve 5 on Fig. 4) when s_p have to decrease sufficiently as a result of increasing the surface barrier for electrons. As it is evident from this relationship, the contribution of surface recombination of photogenerated carriers into decreasing η_i take place in the wide area of potentials. The value s_p decreases after Pt modification in $1.4 \div 2.5$ times depending on electrode potential and reached $(0.4 \div 2.5) \cdot 10^3$ cm/s as it was obtained from data represented in Fig. 4. Such influence of Pt nanoparticles on the recombination may be explained by Pt deposition mainly on

active surface centers and decreasing center concentration. These centers are created by the different kind of surface defects or surface oxides and are the centers of recombination or trapping for charge carriers [9, 10]. Lowering the rate of surface recombination, s_p leads to gain in photopotential on $0.25 \div 0.3$ V that permits fit photoelectrode and MH characteristics for MH charging.

The quantity of hydrogen accumulated was estimated from discharge/charge capacity relation and from hydrogen volume released under MH samples heating. Both methods gave compatible results $50 \div 80$ % for discharge/charge capacity relation.

4. Conclusions

The combination in the one photoelectrochemical cell of GaAs photoanode modified by Pt and cathode based on intermetallic alloy $\text{LaNi}_{5-x}\text{Co}_x$, where $0 \leq x \leq 2.5$, permits photoreduce metal to MH under the action of sunlight. Modification of GaAs by Pt shifted photopotential cathodically of equilibrium MH potentials that is necessary for MH charging. In this case, cathodes with Co content $x \geq 2$ are charged more effectively owing to better kinetic characteristics. The equilibrium MH potential has to be as anodic as possible for more effective charging. Unfortunately, as seen from our investigations, substitution Ni for Co in our alloys does not change the equilibrium potential significantly. Materials with equilibrium hydrogen pressure much lower than atmospheric and equilibrium potential higher than the potential of hydrogen electrode probably will be more prospective for these applications.

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ELECTRONIC STRUCTURE OF CARBON NANOTUBES OF VARIABLE DIAMETER

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Abstract. Equilibrium configurations, total energy, heat of formation, energies of HOMO and LUMO orbitals, density of one-electron states (DOS) of open and semi open carbon nanotubes of variable diameter such types as (6,6)+(6,0), (5,5)+(5,0) and (6,0)+(5,0) are determined in frames of semi-empirical quantum chemistry PM3-method.

Keywords: junctions of carbon nanotubes, variable diameter, molecular simulations, quantum-chemical calculations, modeling.

1. Introduction

The creation of new nanoelectronic devices is not possible without using of elements with anisotropic conductivity. One of the ways to solve the problem is considered here. All calculations are performed in framework of semi empirical PM3-method [1-2].

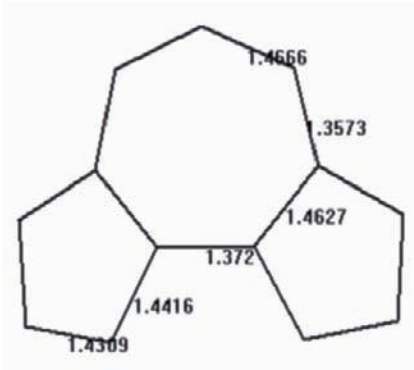
2. Theoretical and computational

The first we give a common description of the construction of carbon nanotubes of variable diameter (CNT VD) which can be obtained in result of junction of two nanotubes with different diameters along their common axes of symmetry (the terms “bottle” is used below due the obvious likeness). As example we consider in details only the construction of (6,6)+(6,0) bottle C_{198} , which is formed by the junction of (6,6) nanotube C_{120} and (6,0) nanotube C_{72} (moreover the ring C_6 take part in forming of the bottle). The length of (6,6) nanotube is 10.94 Å and middle diameter of tube is 8.30 Å (in the region of nanotubes junction diameter is decreased to 7.18 Å, but on the free edge of tube it is increased to 8.55 Å). The length of (6,0) nanotube is 11.17 Å and middle diameter of tube is 4.85 Å (near the place of nanotubes junction diameter is about 5.01 Å, but on the free edge of tube it is only 4.73 Å). The ring C_6 (of diameter near 6.22 Å) is disposed in the region of nanotubes junction, where the belt from six 5-members and six 7-members cycles appears.

One can consider not only open, but semi open and closed bottles also. As it follows directly from the results of semi empirical PM3-calculations the main peculiarities of construction to be described above are typical for all kinds of the (n,n)+(n,0) bottles.

The equilibrium configurations of open and semi open (6,6)+(6,0) CNT and (5,5)+(5,0) CNT are shown in Figs. 1-2. All the results of PM3-calculations are

presented below in tables 1-2, where the following designations are used: E – full energy; ε – mean value of full energy per one carbon atom; ΔH – heat of formation; Δh – heat of formation per one mole of carbon; E_{HOMO} , E_{LUMO} – one-electron energy of highest occupied and lowest unoccupied orbitals, respectively; $E_{gap} = E_{LUMO} - E_{HOMO}$ – the width of forbidden gap.



We introduce the numeration for the lengths of bonds in defective 5- and 7-members cycles $l_1 \dots l_6$ which is based on the principle from bottom to top (from the boundary of the belt with (n,n) CNT to the boundary with (n,0) CNT). The picture on the left illustrates the principle.

2.1. OPEN AND SEMI-OPEN (6,6)+(6,0) AND (5,5)+(5,0) CNTS OF VD

The (n,n)+(n,0) nanotubes of variable diameter can be considered as the result of junction of CNTs with two different types of conductivity: metallic (n,n) CNT and semiconductor (n,0) CNT with forbidden gap near 0.5-1.5 eV. However, the nanotubes of variable diameter are rather the insulators with forbidden gap about 2.5-4 eV.

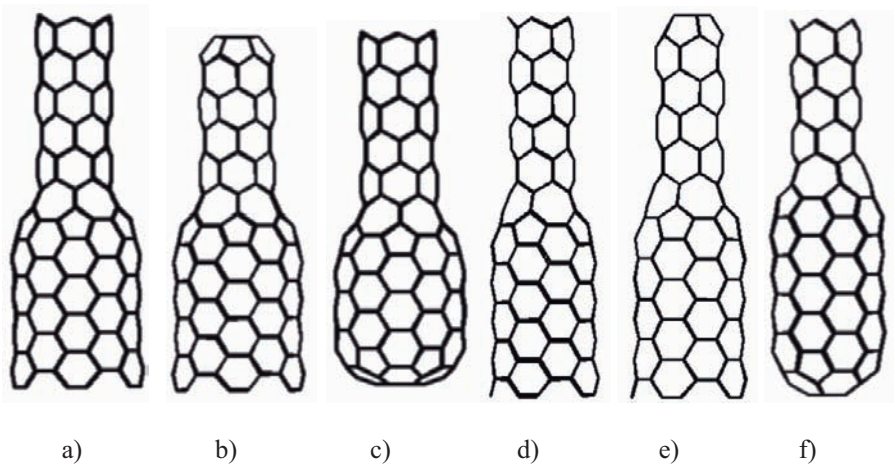


Figure 1. (6,6)+(6,0) CNTs: a) open C_{198} ; b) semi-open C_{192} ; c) semi-open C_{186} . (5,5)+(5,0) CNTs: d) open C_{165} ; e) semi-open C_{160} ; f) semi-open C_{175} .

TABLE 1. Parameters of (6,6)+(6,0) and (5,5)+(5,0) CNTs

	C ₁₉₈	C ₁₉₂	C ₁₈₆	C ₁₆₅	C ₁₆₀	C ₁₇₅
E, eV	-23368	-22670	-21964	-19460	-18878	-20658
ε, eV	-118.0	-118.1	-118.1	-118.0	-118.0	-118.0
ΔH, kcal/mol	2816.6	2507.4	2375.3	2654.7	2415.6	2404.3
Δh, kcal/mol	14.2	13.1	12.8	16.1	15.1	13.7
E _{HOMO} , eV	-7.796	-7.736	-7.323	-8.172	-8.229	-8.237
E _{LUMO} , eV	-4.289	-3.774	-4.338	-4.098	-4.169	-4.112
E _{gap} , eV	3.507	3.962	2.985	4.074	4.060	4.114
l ₁ , Å	1.43	1.44	1.43	1.44	1.44	1.44
l ₂ , Å	1.44	1.45	1.45	1.45	1.45	1.45
l ₃ , Å	1.37	1.37	1.36	1.37	1.37	1.37
l ₄ , Å	1.46	1.47	1.47	1.44	1.47	1.47
l ₅ , Å	1.36	1.36	1.35	1.35	1.35	1.35
l ₆ , Å	1.47	1.48	1.47	1.47	1.47	1.48

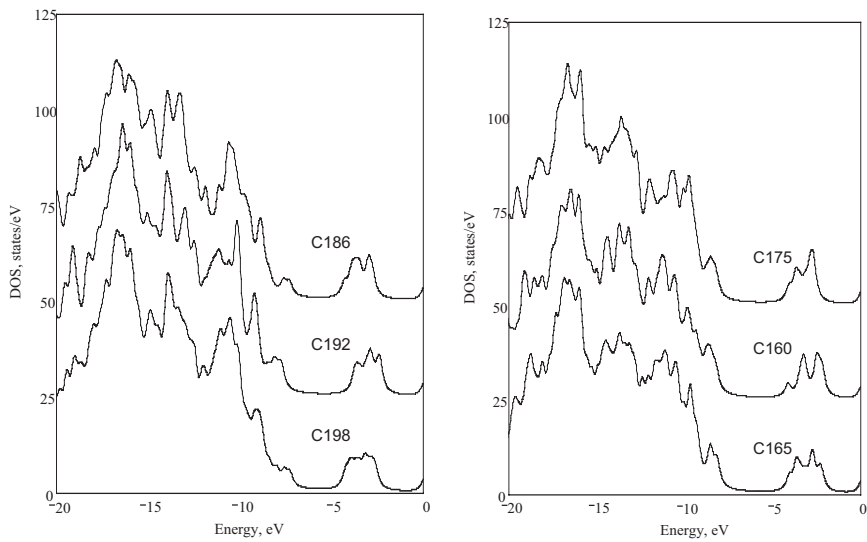


Figure 2. Calculated DOS for (6,6)+(6,0) and (5,5)+(5,0) CNTs.

2.2. OPEN AND SEMI-OPEN (6,0)+(5,0) CNTS

We consider also the nanotubes of variable diameter of such type as $(n+1,0)+(n,0)$. On the boundary between $(n+1,0)$ and $(n,0)$ tubes only one 7-members and one 5-members cycles are created. The axes of $(n+1,0)$ and $(n,0)$ tubes are parallel but they don't coincide, therefore the axis symmetry of junctions in whole is absent.

The same principle (from bottom to top) is used for numeration of the lengths of bonds in pair of defective 5- and 7-members cycles which are disposed in the boundary between $(n+1,0)$ CNT and $(n,0)$ CNT (see the picture on the left).

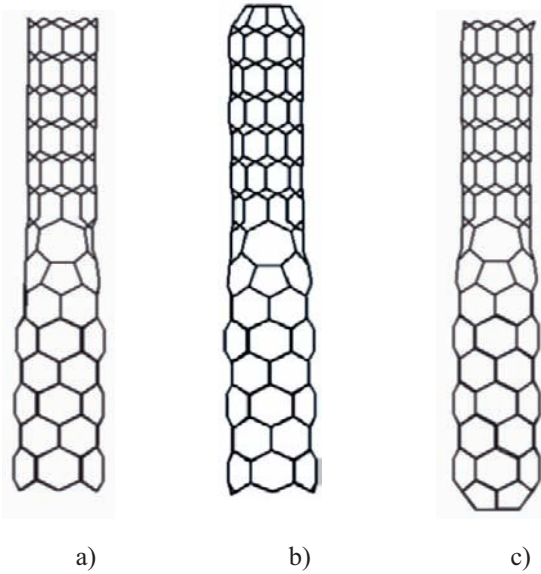
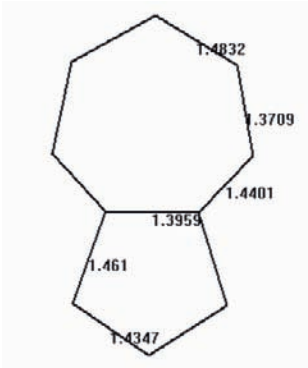


Figure 3. (6,0)+(5,0)-CNTs: a) open C_{165} ; b) semi-open C_{170} ; c) semi-open C_{171} .

TABLE 2. Parameters of (6,0)+(5,0)-CNTs

	C ₁₆₅	C ₁₇₀	C ₁₇₁
E, eV	-19443	-20040	-20162
ε, eV	-117.8	-117.6	-117.9
ΔH, kcal/mol	3049.1	2964.4	2888.7
Δh, kcal/mol	18.5	17.4	16.9
E _{HOMO} , eV	-7.943	-7.987	-7.848
E _{LUMO} , eV	-4.227	-4.169	-4.158
E _{gap} , eV	3.676	3.818	3.690
l ₁ , Å	1.43	1.43	1.44
l ₂ , Å	1.46	1.46	1.46
l ₃ , Å	1.40	1.40	1.35
l ₄ , Å	1.44	1.44	1.44
l ₅ , Å	1.37	1.37	1.38
l ₆ , Å	1.48	1.48	1.48

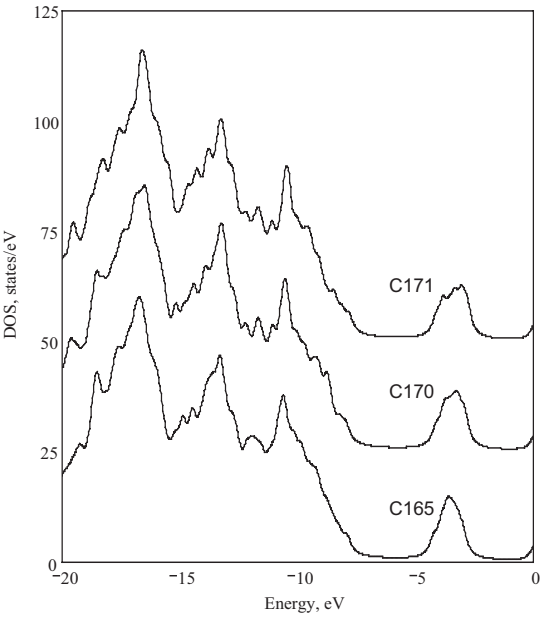


Figure 4. Calculated DOS for (6,0)+(5,0)-CNTs.

The results of our calculations are in a reasonable accordance with the data of recently papers [3-5] devoted to research of the same problems. It's clear that nanotubes of variable diameter of such kind must possess anisotropic conductivity and therefore can be used as switching elements in future nanodevices [6-7].

3. Conclusions

The results of semi-empirical PM3 calculations confirm the possibility of existence of the different types of nanotubes of variable diameter.

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CUBIC POLYMERIZED STRUCTURES OF SMALL FULLERENES C₂₀, C₂₄, C₂₈, C₃₂

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Abstract. Geometrical parameters, total energy, heat of formation, energies of HOMO and LUMO orbitals, density of one-electron states (DOS) are determined by using of semi-empirical quantum chemistry PM3-method for isolated molecules C_n, dimers (C_n)₂ and cuban-like clusters (C_n)₈ for n = 20, 24, 28, 32. The results of calculations allow assuming the existence of polymerized cubic crystal structure on base of all considered small fullerenes.

Keywords: polymerized fullerenes, clusters and crystal structures, cubic symmetry, quantum-chemical calculations.

1. Introduction

The first discovered solid phase of fullerenes C₆₀ represents typical molecular crystal. Later it was established that high pressure applied to solid C₆₀ at high temperature induces polymerization of C₆₀ [1-2]. Using the computer modeling methods allows confirming the existence of at least three different planar polymerized structures of fullerene C₆₀ with coordination numbers 2, 4, 6, and besides the values 4 and 6 are more probable ones.

Now polymerized structures on basis of big and small fullerenes with different dimensionality and symmetry are the subjects a lot of theoretical and experimental investigations.

The paper continues our earlier researches [3] and the main purpose is theoretical investigations of possibility of existence of stable high symmetry polymerized structures of small fullerenes C₂₀, C₂₄, C₂₈ and C₃₂.

2. Theoretical and computational

The geometrical parameters of equilibrium configurations of small fullerenes isolated molecules C_n, their dimers (C_n)₂ and cuban-like clusters (C_n)₈ are obtained for n = 20, 24, 28, 32. The cuban' like clusters can be considered as fragments of polymerized crystal structures with simple cubic symmetry. Total energy, heat of formation, energies of HOMO and LUMO orbitals, density of one-electron states (DOS) are determined for equilibrium configurations of all these objects. All the computations are performed by help of pocket PC Gamess in frames of optimized semi-empirical PM3-basis [4-5].

The results of calculations are presented below.

2.1. MOLECULE C_{20} , DIMER $(C_{20})_2$ AND CLUSTER $(C_{20})_8$

Molecule C_{20} is the smallest one from all the fullerenes [9] and has the form of dodecahedra (point symmetry group Y_h). We consider here only polymerized structures (clusters) which are formed by the pairs of bridge like bonds directed along molecules second order axes. The clusters formation is accompanied by the distortion of the geometry of molecules that leads as sequence to decreasing the symmetry both molecule and cluster (for example the symmetry group of cluster $(C_{20})_8$ is only D_{2h}).

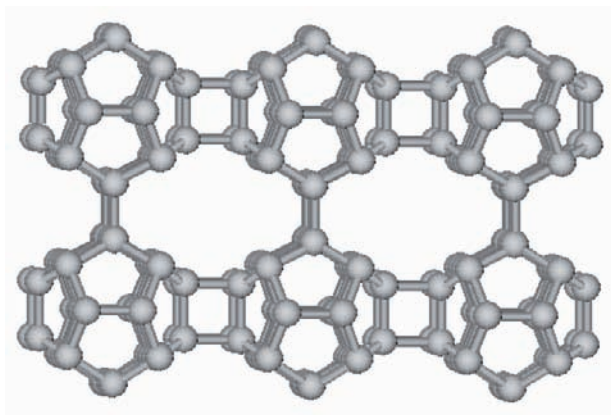


Figure 1. Fragment of polymerized cubic phase C_{20} .

In the Table 1 there are collected the most important characteristics of the objects under studying: total energy E , heat of formation ΔH , and energies of intermolecular bonds per one bond, one fullerene molecule C_{20} and one carbon atom. Although the energy of each of intermolecular bonds decrease with increasing of the number of molecules in cluster but the intermolecular bonds energy per one molecule (or per one carbon atom) and therefore stability of structure increase with growth of cluster size.

The values of HOMO and LUMO orbitals given in the table allow estimating roughly the width of forbidden gap as difference of these values. To proceed from this point one can suppose that cubic phase of polymerized C_{20} is insulator with forbidden gap about 4 eV.

In the Table there are given also the length of intramolecular and intermolecular bonds. The following designations are used: l_1 – the length of intramolecular bond between any pair of atoms which take part in forming of intermolecular bonds; l_2 – the length of intramolecular bond between one of those atoms and any other of the nearest neighbors. The changes of the other bonds lengths are not so essential although the molecules geometry distortion in whole is observed. The results of our calculations allows to conclude about the possibility of polymerization of C_{20} in simple cubic lattice with period about $a = 5.580 \text{ \AA}$.

TABLE 1. Calculated parameters of fullerene C_{20} , dimer $(C_{20})_2$ and cuban-like cluster $(C_{20})_8$

	C_{20}	$(C_{20})_2$	$(C_{20})_8$
E, eV	-2340	-4687	-18777
ΔH , kcal/mol	754.5	1358.2	4733.9
ΔE_b , eV/bond	—	3.272	2.353
ΔE_m , eV/mlc.	—	3.272	7.060
ΔE_a , eV/atom	—	0.164	0.353
E_{HOMO} , eV	-8.934	-9.113	-7.951
E_{LUMO} , eV	-3.603	-3.214	-3.567
E_{gap} , eV	5.331	5.899	4.384
l_1 , Å	1.495	1.528	1.516
l_2 , Å	1.495	1.646	1.647
l_{inter} , Å	—	1.510	1.513

2.2. MOLECULE C_{24} , DIMER $(C_{24})_2$ AND CLUSTER $(C_{24})_8$

The interest to polymerized structures on base of fullerene C_{24} is stimulated by remarkable results of outstanding paper [8]. The authors of [8] use the quantum solid state calculations for to explain the crystal structure of cubic graphite synthesized for the first time at low temperatures ($T = 77$ K or $T = 276$ K) and pressure $P > 150$ kbar [10]. We repeat the calculations performed in [8] but only in cluster approximations and moreover in the frameworks of semi-empirical PM3-method. Must be noted that isolated molecule C_{24} (which is the basic building unit of cubic graphite) is not similar to the standard fullerene molecules containing only hexagonal and pentagonal faces. Besides eight hexagonal faces molecule C_{24} contains six squares. Just the atoms in vertex of squares take part in forming of intermolecular bonds in cubic graphite and clusters on the base of C_{24} .

Some the results of calculations (total energy, heat of formation, HOMO and LUMO orbitals energies and so on) are collected in Table 2.

The exceptional large value of forbidden gap width seems to be any doubtful. Perhaps it means that not all of the calculations results obtained for small clusters can be used for prediction of crystal structures properties. Must be noted that calculated bonds lengths in squares and hexagons and period of crystal lattice (1.607 Å, 1.452 Å, 5.894 Å) differ from the values (1.503 Å, 1.380 Å, 5.545 Å), obtained in [8]. However one can not expect the better accordance from the results of clusters calculations performed moreover in the frames of semi-empirical PM3-basis.

2.3. MOLECULE C_{28} , DIMER $(C_{28})_2$ AND CLUSTER $(C_{28})_8$

For the first time the small fullerene molecule C_{28} was discovered in structure of endohedral complex $U@C_{28}$ [11]. The entire first attempts to extract the isolated molecule C_{28} in purely kind failed. Theoretical calculations show that isolated molecule C_{28} is radical with 4 non-paired electrons ($S = 2$), localized on atoms, disposed in vertexes which are common for each three neighboring pentagons. Exactly this fact explains the high activity of isolated molecule C_{28} and unsuccessful attempts to get it in purely kind.

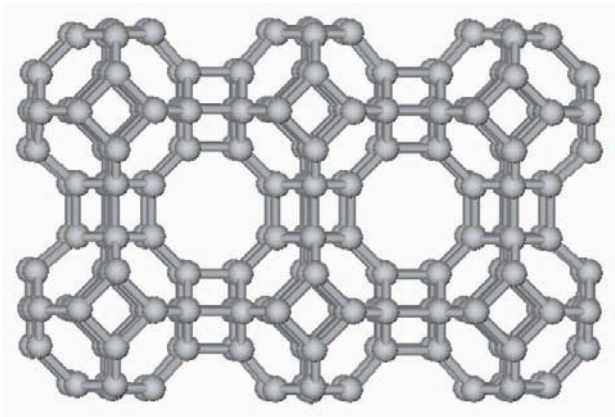


Figure 2. Fragment of polymerized cubic phase C_{24} .

TABLE 2. Calculated parameters of fullerene C_{24} , dimer $(C_{24})_2$ and cuban-like cluster $(C_{24})_8$

	C_{24}	$(C_{24})_2$	$(C_{24})_8$
E, eV	-2813	-5628	-22559
ΔH , kcal/mol	786.2	1539.5	5076.4
ΔE_b , eV/bond	–	0.356	1.096
ΔE_m , eV/mlc.	–	0.712	6.574
ΔE_a , eV/atom	–	0.030	0.274
E_{HOMO} , eV	-9.570	-9.140	-9.606
E_{LUMO} , eV	-2.511	-3.050	-2.343
E_{gap} , eV	7.059	6.090	7.257
l_1 , Å	1.494	1.622	1.607
l_2 , Å	1.369	1.450	1.452
l_{inter} , Å	–	1.545	1.550

The isolated molecule C_{28} point symmetry group is T_d . The 42 covalent bonds of three different types take part in forming of the cage of molecule:

- 1. 6 bonds with length 1.520 Å, which connect the vertexes of each pair of hexagons;
- 2. 24 bonds with length 1.427 Å, which are the verges of four hexagons;
- 3. 12 bonds with length 1.458 Å, which are joined in four vertexes, common for each three neighboring pentagons.

Just the atoms in vertexes of first type bonds take part in forming bridge' like intermolecular bonds in clusters on base of C_{28} .

The results of calculations allow supposing the existence of polymerized FCC crystal phase of C_{28} with period of the lattice $a = 13.080$ Å (the space symmetry group coincides with symmetry group of crystal NaCl and period of lattice is twice more than distances between the centers of neighboring molecules). One can expect the solid phase of C_{28} is insulator with forbidden gap width about 2 eV. The results of our calculations don't contradict to the data of earlier theoretical searches [12-13].

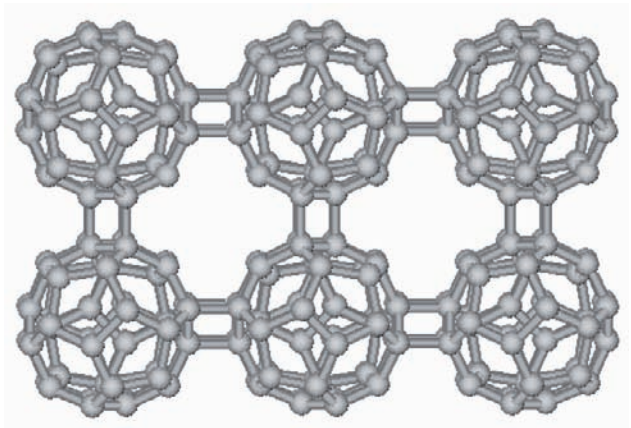


Figure 3. Fragment of polymerized cubic phase C_{28} .

TABLE 3. Calculated parameters of fullerene C_{28} , dimer $(C_{28})_2$ and cuban-like cluster $(C_{28})_8$

	C_{28}	$(C_{28})_2$	$(C_{28})_8$
E , eV	-3286	-6579	-26339
ΔH , kcal/mol	824.6	1495.1	5439.5
ΔE_b , eV/bond	—	3.343	2.092
ΔE_m , eV/mlc.	—	3.343	6.275
ΔE_a , eV/atom	—	0.119	0.224
E_{HOMO} , eV	-8.485	-9.045	-7.107
E_{LUMO} , eV	-4.550	-3.679	-5.216
E_{gap} , eV	3.935	5.366	1.891
l_1 , Å	1.520	1.693	1.698
l_2 , Å	1.427	1.506	1.502
l_3 , Å	1.458	1.458	1.454
l_{inter} , Å	—	1.524	1.526

2.4. MOLECULE C_{32} , DIMER $(C_{32})_2$ AND CLUSTER $(C_{32})_8$

In analogous with the clusters based on C_{24} one can consider the hypothetical structures based on one of the exotical form of molecules C_{32} .

Among all the isomers of fullerenes C_{32} we choice the molecule with cubic point symmetry group O_h . The molecule cage is formed by 12 hexagonal and 6 square faces. The atoms disposed in vertex of squares take part in forming of intermolecular bonds in dimer $(C_{32})_2$ and cuban-like cluster $(C_{32})_8$.

The results of calculations are presented in Table 4. The energy of each of intermolecular bonds decrease with increasing of the number of molecules in cluster but the intermolecular bonds energy per one molecule (or per one carbon atom) and as sequence stability of structure increase with growth of cluster size.

In accordance with obtained results one can to suppose that simple cubic phase of C_{32} is insulator with forbidden gap width about 1.5 eV and crystal lattice period $a = 6.749 \text{ \AA}$.

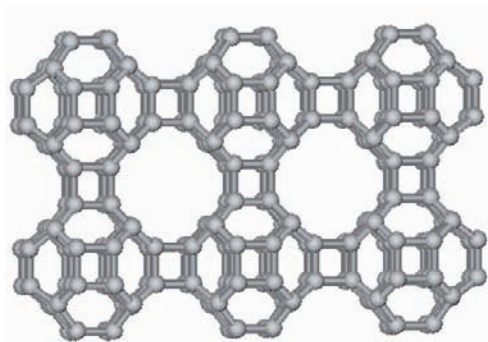


Figure 4. Fragment of polymerized cubic phase C_{32} .

TABLE 4. Calculated parameters of fullerene C_{32} , dimer $(C_{32})_2$ and cuban-like cluster $(C_{32})_8$

	C_{32}	$(C_{32})_2$	$(C_{32})_8$
E, eV	-3759	-7518	-30109
ΔH , kcal/mol	1032.1	1734.6	5978.5
ΔE_b , eV/bond	—	3.573	1.983
ΔE_m , eV/mlc.	—	7.147	11.895
ΔE_a , eV/atom	—	0.223	0.372
E_{HOMO} , eV	-7.551	-8.593	-6.433
E_{LUMO} , eV	-4.337	-2.944	-5.094
E_{gap} , eV	3.214	5.491	1.339
l_1 , $\text{\AA}$	1.403	1.605	1.605
l_2 , $\text{\AA}$	1.419	1.475	1.472
l_{inter} , $\text{\AA}$	—	1.552	1.5558

3. Conclusions

The results PM3-calculations of the geometry and electronic structures cuban-like clusters $(C_n)_8$ (for $n = 20, 24, 28, 32$) show the possibility of existence of polymerized cubic crystal structures on the base of small fullerenes.

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ELECTRONIC STRUCTURE OF T-JUNCTIONS OF CARBON NANOTUBES

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Abstract. Equilibrium configurations, total energies, heats of formation, energies of HOMO and LUMO states, densities of one-electron states (DOS) and IR spectra of CNTs T-junctions of the various types are calculated by employing of PC Gamess version of semi-empirical quantum chemistry PM3-method.

Keywords: T-junctions of carbon nanotubes, defects, topological restrictions, molecular simulations, quantum-chemical calculations.

1. Introduction

In the paper we continue the researches started in [1] where the possibility of existence of T-junctions of (6,6) CNT with graphite monolayer was shown. Here some samples of T-junctions of carbon zigzag and armchair CNTs are investigated. Experimental and theoretical aspects of perspectives of using of CNT T-junctions as elements of future nanoscale electronic devices are considered earlier in [4-10].

2. Theoretical and computational

In the framework of semi-empirical method PM3 (worked out by Stewart [2,3] especially for calculation of electronic structure of carbon-contained organic molecules) the calculations of equilibrium configurations, full energy, heat of formation and electronic structure of different types of T-junctions of carbon zigzag and armchair nanotubes were done.

The densities of one-electron states (DOS) are calculated for all considered T-junctions also.

To extract Hessian (matrix of second derivatives of total energy on atoms coordinates) from the results of calculations performed in frames of PC Gamess version of PM3-method one can compute the frequencies of all self vibration modes as good as intensities of infrared (IR) spectra of T-junctions and compare this spectra with computed IR spectra of the ideal nanotubes.

Only the part of the results of computations for some of the most stable T-junctions is presented here. It should be noted that all our attempts to find the stable configurations of T-junctions such type as zigzag + armchair failed.

2.1. EQUILIBRIUM CONFIGURATIONS AND IR SPECTRA

a) T-junctions of the type armchair + armchair

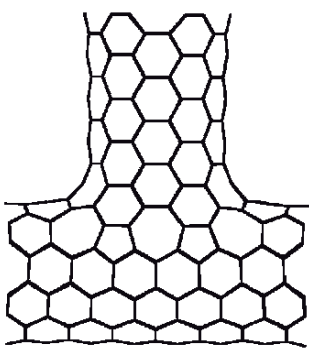


Figure 1. (6,6)+(6,6) T-junction C₂₄₆.

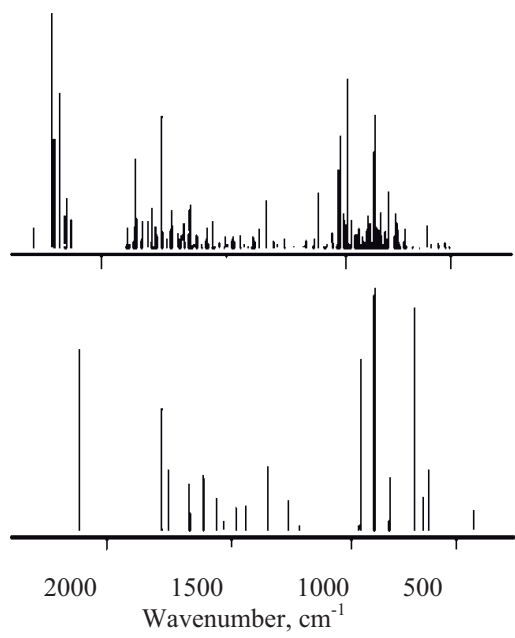


Figure 2. IR spectra of (6,6)+(6,6) T-junction (upper spectrum) and (6,6) CNT (lower spectrum).

b) *T-junctions of the type armchair + zigzag*

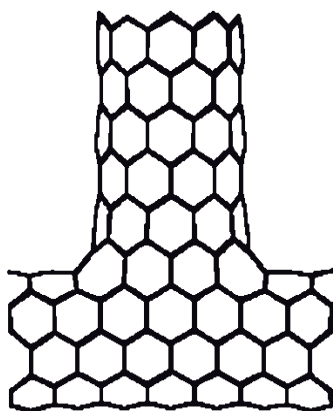


Figure 3. T-junction C_{256} of the type (5,5)+(10,0).

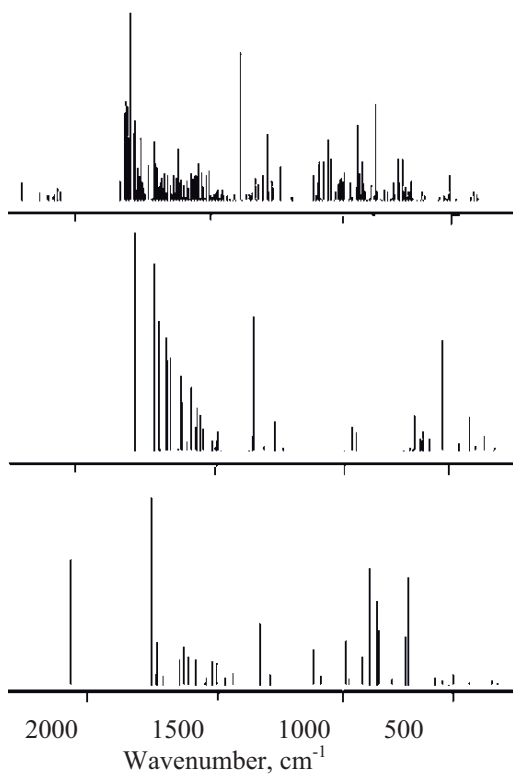


Figure 4. IR spectra of (5,5)+(10,0) T-junction (upper spectrum) and (5,5) and (10,0) CNTs (two lower spectrum).

c) *T-junctions of the type zigzag + zigzag*

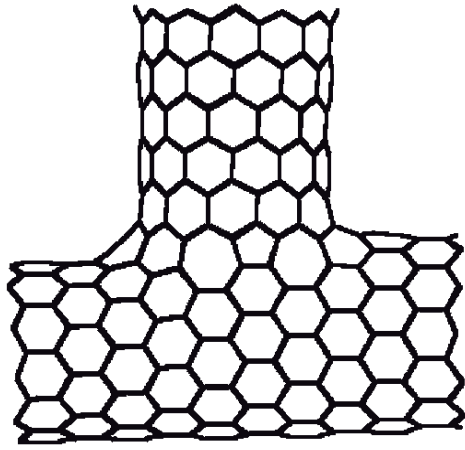


Figure 5. T-junction C_{384} of the type $(12,0)+(12,0)$.

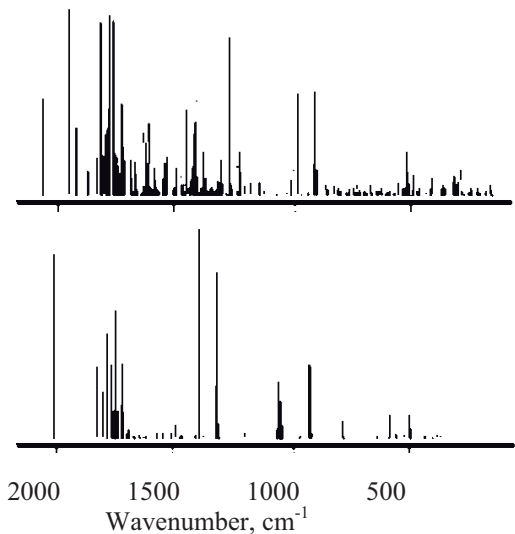


Figure 6. IR spectra of $(12,0)+(12,0)$ T-junction (upper spectrum) and $(12,0)$ CNT (lower spectrum).

The IR spectra of all the T-junctions inherit in whole the shape of IR spectra of ideal CNTs but in comparison with the last ones they have more reach structures and are shifted in the region of higher frequencies (wavenumbers). These facts can be easy explained as the result of interactions of vibration modes of CNTs which take part in forming of the junctions on the one hand and contributions of the defective cycle's vibrations on the other hand.

The results of our calculation for IR spectra of ideal CNTs aren't in contradictions with the data of previous investigations [11-15]. The only difference is concluded in appearance of additional peaks in high frequency region which are connected with the vibrations of carbon atoms disposed on the edges of tubes (we consider only the fragments of ideal tubes of finite length).

2.2. TOTAL ENERGIES, HEATS OF FORMATION AND ELECTRONIC STRUCTURES

There are presented here some the results of PM3 calculations of total energies, heats of formation, and energies of HOMO and LUMO states, and shape of DOS also for the entire described junctions. The following designations are used in the table below: ε – mean value of full energy per one carbon atom; Δh – heat of formation per one mole of carbon; E_{HOMO} , E_{LUMO} – energy of highest occupied and lowest unoccupied orbitals; $E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ – the width of forbidden gap (one must keep in mind the conventional character of the last definition).

The direct comparison shows clearly that shapes of DOS of T-junctions (for exception of region near forbidden gap) repeat in whole the shapes of DOS of CNTs taking part in forming of junctions.

TABLE 1. Calculated characteristics of T-junctions

	C ₂₄₆	C ₂₅₆	C ₃₈₄
ε , eV	-117.23	-117.21	-117.25
Δh , kcal/mol	13.20	13.77	12.78
E_{HOMO} , eV	-7.973	-7.461	-7.883
E_{LUMO} , eV	-4.815	-4.653	-4.474
E_{gap} , eV	3.158	2.808	3.409

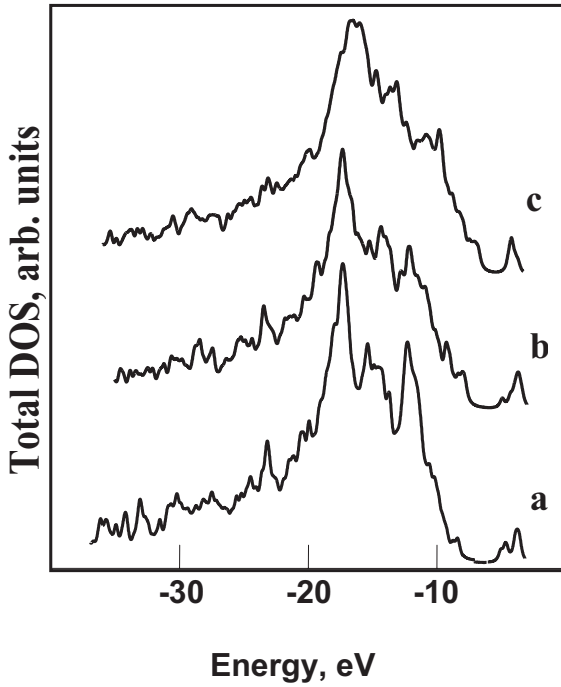


Figure 7. Calculated DOS of T-junctions: a) (6,6)+(6,6); b) (5,5)+(10,0); c) (12,0)+(12,0).

2.3. EULER-POINCARÉ CHARACTERISTIC AND SOME TOPOLOGICAL RESTRICTIONS

All the discussed structures can be considered as the result of junctions any number of zigzag or armchair CNTs. Therefore the components of the edge of similar cage structure are either edge of zigzag or armchair CNT. All the inner carbon atoms in quasi-planar cage structure are connected with three nearest neighbors, but atoms disposed on the edge of structure are connected only with two nearest neighbors.

Let introduce the designations m_s for numbers of s -angle's faces, which take part in forming of cage structure (in the structures under studying s can get the values 5, 6, 7, 8). Let suppose also that the edge of the structure contain p components of zigzag type and q components of armchair type. Then numbers of vertexes, verges and faces in the structure can be determined by the following formulas:

$$\Gamma_0 = \frac{1}{3} \cdot \sum_{s=5}^8 s \cdot m_s + \sum_{i=1}^p n_i + 2 \cdot \sum_{j=1}^q n'_j \quad (1)$$

$$\Gamma_1 = \frac{1}{2} \cdot \sum_{s=5}^8 s \cdot m_s + \sum_{i=1}^p n_i + 2 \cdot \sum_{j=1}^q n'_j \quad (2)$$

$$\Gamma_2 = \sum_{s=5}^8 m_s \quad (3)$$

From topological point of view similar structure is not any other than 3D-sphere with $p + q$ holes, Euler-Poincare characteristic of which is equal to

$$\chi = 2 - p - q. \quad (4)$$

On the other hand Euler-Poincare characteristic of the any cage structure can be evaluated as the alternating sum of numbers of vertexes, verges and faces in the structure:

$$\chi = \Gamma_1 - \Gamma_2 + \Gamma_3 = \sum_{s=5}^8 \left(1 - \frac{s}{6} \right) \cdot m_s. \quad (5)$$

To compare the formulas (4) and (5) one can obtain the relation between the numbers of the faces of the different kinds:

$$m_5 - m_7 - 2m_8 = 6 \cdot (2 - p - q). \quad (6)$$

For T-junctions of CNTs of any types the sum $p + q = 3$ and therefore Euler-Poincare index get value $\chi = -1$ and the right hand side of relation (6) is equal to -6 .

TABLE 2. Geometrical parameters of T-junctions

	C_{246}	C_{256}	C_{384}
m_5	4	0	2
m_6	90	106	164
m_7	10	6	6
m_8	0	0	1
p	0	1	3
q	3	2	0
Γ_0	246	256	384
Γ_1	351	369	558
Γ_2	104	112	173

The data presented in Table 2 show clearly that all the considered above T-junctions satisfy to the topological restriction (6). It must be especially noted that only the topological restrictions can't be the obstacle to the creation of the stable configurations of zigzag + armchair T-junctions. All of our experiences allows to suppose that true reason concludes in the bad geometrical compatibility of based zigzag CNT with branch armchair CNT that lead to the strong distortion of symmetry and geometry of CNTs at all attempts to connect its.

3. Conclusions

Equilibrium configurations, total energies, heats of formation, the electronic structure, the self vibrations frequencies and IR spectra of the various possible types of T-junctions are computed by employing of PC Gamess version of semi-empirical PM3-method. The results of our calculations in whole are in a good agreement with published earlier the data of theoretical and experimental researches devoted to the studying of T-junctions.

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METAL-CARBON NANOSTRUCTURED MEMBRANE CATALYSTS

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Abstract. The membrane catalysts possess a selective permeability for one of the reagents. The carbon materials got the increasing value in processes of membrane for gas separation due to their high selectivity and permeability, high hydrophobicity and stability in corrosive and high-temperature operations. At the same time carbon materials are widely known supports of metal catalysts. The present work is the first sample of development of the methods of preparation of carbon membrane catalysts with metal nanoparticles in a carbon membrane matrix. The other granulated rhenium-carbon catalyst was obtained for the first time by high-temperature destruction of copolymers. It is shown, that both catalysts are active in hydrocarbons dehydrogenation and demand considerably the smaller maintenance of metal, than the traditional catalysts put on coal, with other things being equal.

Keywords: membrane catalyst, nanoparticle, carbon

1. Introduction

The membrane catalysts are offered the decades ago and are attractive for the intensification of some processes of chemical, petrochemical, medical and the food-processing industry and essential increase of selectivity of catalysts due to their selective permeability for only one of reagents [1].

The carbon materials attract the increasing interest of membrane scientists because of their high selectivity and permeability, high hydrophobicity and stability in corrosive and high-temperature operations. Recently many papers were published considering last achievements in the field of carbon membranes for gas separation [2-5]. In particular, such membranes can be produced by pyrolyzing a polymeric precursor in a controlled condition. The one of most usable polymer for this goal is polyacrylonitrile (PAN) [6]. Some types of carbon membranes were obtained as a thin film on a porous material by the carbonization of polymeric predecessors [7]. Publications about carbon membrane catalysts are not found up to now.

On the other hand the carbon materials are widely known supports of metal catalysts from of old. It has been shown, that the carbon supports increase the dehydrogenative properties of the metal catalysts due to the epitaxial changing of metal crystal structure providing their structural relevance with reacting molecules [8].

The present work is the first attempt to develop the methods of preparation of carbon membrane catalysts with metal nanoparticles in a carbon membrane matrix.

The activity of obtained composite membrane catalysts is investigated in the model reactions of hydrocarbons dehydrogenation.

2. Experimental

We pioneered the use a noncoherent IR radiation for a formation of the metal - carbon film on a surface of porous inorganic support. In this research the film was obtained from a mixture PAN and ammonium perrenate solutions in dimethylformamide on the surface of the porous stainless steel.

Then the film was annealed by intensive IR-radiation and was quenched up to a room temperature with a rate 10-20 K/s. The intensity of IR-radiation was controlled by the resulting temperature of a film (950-1050 K). The halogenic lamps KG - 220 ($\lambda = 0.9 - 1.7$ microns) were used as an IR-radiation source. The optimum size of molecular mass of polymer (100000 – 200000) allowed to obtain the stable defectless film on the porous substrate.

IR-radiation influences selectively on oscillatory energy of separate groups of a PAN macromolecule, allowing operating in the certain limits of the chemical transformations, leading to formation of a carbon material. Figure 1 shows the principal scheme of PAN film conversion to carbon film.

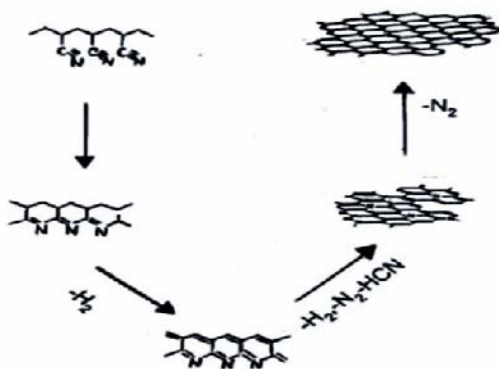


Figure 1. The principal scheme of PAN film conversion to carbon film at IR noncoherent radiation.

X-Ray phase analysis evidences several amorphous phases in the structure of IR-irradiated PAN [9]. The basic amorphous carbon phases are: intermediate phase, corresponding to a wide halo with a half width of $\sim 15^\circ 2\theta$ and $d_{\max} = 3$ Å; graphite-like phase is identified from $d_{002} = 3.35-3.80$ Å; the polynaphtene phase ($d = 4.7$ Å). Graphite-like phase is amorphous due to irregular shifting graphite network one relatively to another and small dimensions of crystallite coherent scattering regions. The content of graphite-like phase at the IR-radiation temperature 1073 K is 100%. On the basis of analysis of X-ray diffraction, electron microscopy and Auger spectroscopy results was shown that structure of amorphous carbon material is inhomogeneous. There are nanocrystal incorporations which dimensions are no more than 100 nm [9].

The reduction of rhenium salt in a PAN matrix and the formation of the polyconjugated polymer system proceed simultaneously and interdependently during IR-pyrolysis of a film. As result the thin film of carbon with ultra dispersed metal particles is formed on a surface of porous support (Fig. 2). The thickness of defectless Re-containing carbon film was 300 – 500 nm. The size of metallic particles was proved to be from 3 to 10 nm. The average content of rhenium in a metal-carbon composition was about 5 mass %.

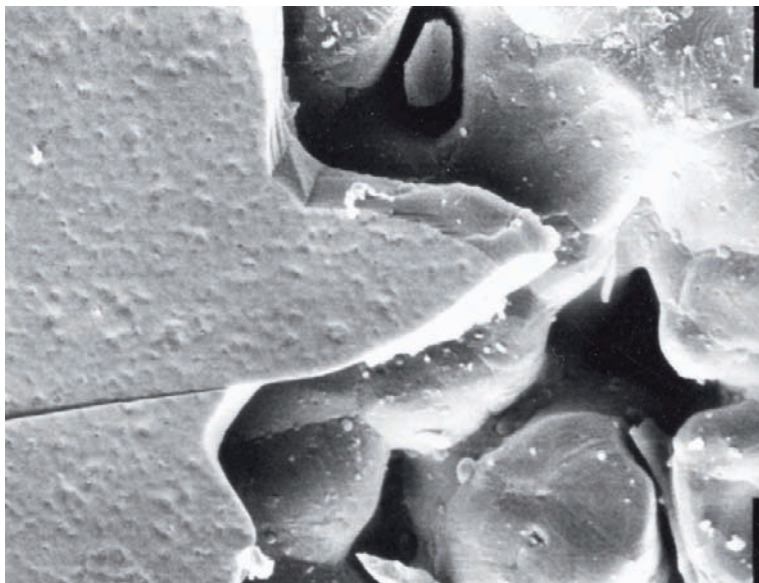


Figure 2. Scanning electron micrograph of a cross section of the porous stainless steel supported Re-containing carbon membrane. Magnification is x3000. 1 – the stainless support; 2 – the Re-carbon layer; 3- Re-particles on the membrane surface.

The granulated rhenium catalyst on the carbon support has been obtained in another way. The pyrolysis of a copolymer of acrylonitrile and divinylbenzene was carried out at the temperatures of 1150-1250 K. The obtained carbonisate, soaked preliminary by ammonium perrhenate (the maximal rhenium loading was 7 mass. per cent in recalculation on metal), was subjected to the further heat treatment in an inert atmosphere at 1450 K. The heating was carried out step by step. The gradual heating up to 950 K caused a decomposition of ammonium perrhenate to surface oxides in pores of carbon matrix. Then, the interaction of metal oxide with a carbon matrix, including the chemical and crystallochemical reactions, occurring frequently in parallel, give a Re-organic compound. The loss of nitrogen up to the maintenance of 1-2 % are observed at the temperatures as high as 1250 K. Simultaneously carbon reduces rhenium oxide to the metal rhenium and oxygen evolved interacts with a carbon surface, causing a porosity.

Crystal structure of this catalyst proved to be similar to α -silica structure ($a = 4.90$ Å, $c = 5.4$ Å), considerably distinguished from parameters of the lattice of graphite ($a = 2.46$ Å, $c = 5.7$ Å), and from that of rhenium carbide lattice

($a = 2.74 - 2.81$ Å). Carbide presence at the catalyst is not observed, as its decomposition on free metal and carbon takes place in annealing process. The "secondary carbon" formed has crystal graphite-like structure, and rhenium presents in intralayer space of graphite fragments, deforming considerably its hexagonal lattice.

X-ray diffraction pattern of the catalyst (Fig. 3) has no responses of crystal rhenium in the area of $2\theta = 2.0 \div 42.9$ grad. It does mean that atoms of rhenium present between the layers of graphite structure. At the same time XPS spectra contain two maxima at the bonding energy of 1.48 and 1.84 eV, characteristic for rhenium.

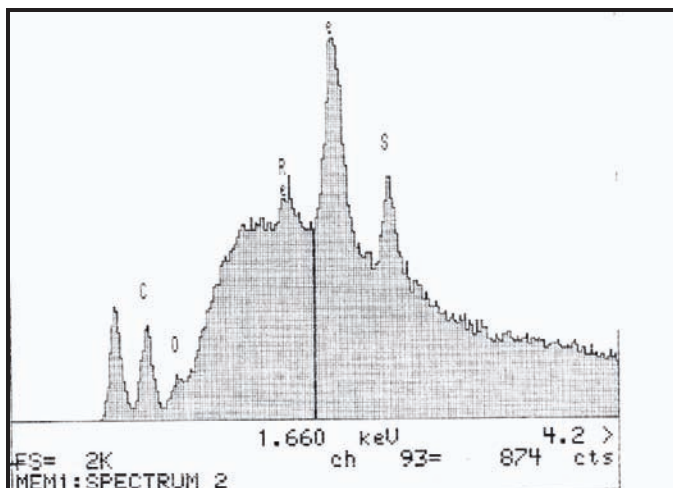


Figure 3. XRD spectrum of the catalyst, obtained from copolymer carbonisate and ammonium perhenate.

The catalytic activity of membrane catalyst, obtained by IR-pyrolysis of PAN and ammonium perrhenate, was studied in the flow membrane reactor in a model reaction of cyclohexane dehydrogenation at the temperatures from 500 to 700 K.

The sheet of porous stainless steel with Re-carbon deposited film divided membrane reactor onto two equal parts. Cyclohexane vapors were fed to the surface of membrane with Re-carbon film (reaction part of membrane reactor) in argon flow from the thermostated bubbler. The second part of reactor was flowed by argon and used for the removal of hydrogen, diffused through a membrane catalyst from the reaction zone. The products of reaction were benzene and hydrogen.

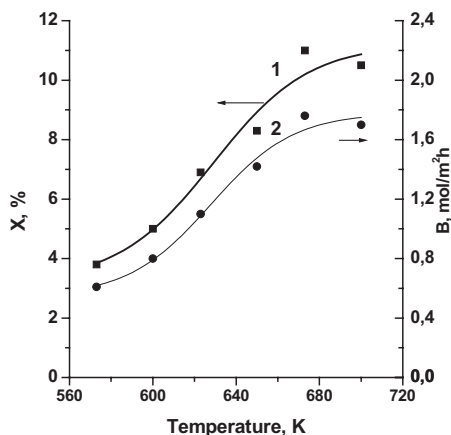


Figure 4. The temperature dependences of cyclohexane conversion (curve 1) and benzene yield (curve 2) for the membrane catalyst, obtained by IR-pyrolysis of PAN and ammonium perrhenate, containing 5 mass % of Re.

Figure 4 shows the temperature dependences of cyclohexane conversion (curve 1) and benzene yield (curve 2). The maximal benzene productivity was 1.76 mol/m²h at 673 K with the catalyst containing 5 % Re. The usual Re/C catalysts require Re loading as much as 30% for achievement the similar activity at such operation conditions [8]. This may be explained by the membrane form of catalyst, used in this work, in spite of the absence of absolute permselectivity of the membrane.

The activity of granulated rhenium catalyst, obtained from copolymer carbonisate, has been investigated in reactions of cyclohexane or ethylbenzene dehydrogenation in bed –packed quartz tube reactor at the plug flow conditions at temperatures from 650 to 900 K, the reagents feed of 30 - 100 ml/min and initial hydrocarbons partial pressure of 0.5 kPa.

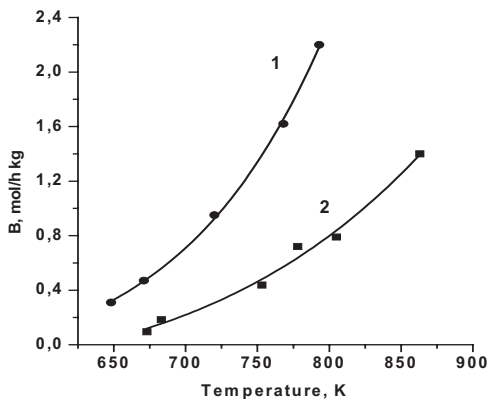


Figure 5. The temperature dependences of benzene (curve 1) and styrene (curve 2) yields at cyclohexane and ethylbenzene dehydrogenation, respectively, on the catalyst, obtained from copolymer carbonisate, containing 7 mass per cent of Re.

As can be seen from Fig. 5, the maximal yield of benzene from cyclohexane was 2.3mol/kg h. The catalysts stable work was observed for a long time without regenerations at high conversion of initial reagents.

High catalytic activity of catalysts in reactions of reception of cyclohexane and ethylbenzene dehydrogenation simultaneously with expensive active metal economy, high mechanical durability, and an opportunity of regeneration of the catalyst are achieved due to creation of optimum structure of carbonized material already on the synthesis stage.

3. Conclusions

1. The composite membranes containing on a surface a thin carbon film with a metal phase were obtained for the first time by using of the noncoherent IR-radiation. It is shown, that such catalysts demand considerably the smaller maintenance of metal, than the traditional catalysts put on coal, with other things being equal.
2. The granulated catalyst containing up to 7 mass. per cent of rhenium in a porous carbon matrix was obtained for the first time by high-temperature destruction of copolymers.

Acknowledgements

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CARBON UNDER PRESSURE AND RADIATION

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Abstract. Structure changes in amorphous phases of different modifications of carbon (diamond, graphite, fullerene) have been investigated by means of neutron and x-ray diffraction under irradiation and pressure. Polyamorphic transition (diamond-like - graphite-like phases) was found in irradiated diamonds by density change. It is shown that radiation amorphization of graphite might be connected with softening of the vibration modes at volume increasing. Polyamorphic transition has been established in amorphous fullerenes at high temperature annealing after radiation or ball milling amorphization.

Keywords: diamond, graphite, fullerene, high pressure, neutron scattering, crystal structure

Investigation of structural changes and phase transitions that occur in glasses and fluids upon changing volume is of great current interest [1]. These changes have been observed in various systems, such as GeO_2 , SiO_2 , H_2O , etc. [2–8]. They are manifested as a change in the radial distribution function due to high pressures and are associated with an increase in the coordination number in the first coordination sphere (from four to six in GeO_2) in systems where it is small. A similar phenomenon, which is manifested in the existence of different structural forms of a disordered state and is called polyamorphism, can be expected for other methods of volume change, in particular, upon the irradiation of crystals after its radiation amorphization. An increase of volume upon reactor irradiation is large and can reach several tens of percent for sufficiently high neutron fluences [9], which is equivalent to a “negative” pressure of several tens or even hundreds of gigapascals. In light of this circumstance, aim of this work is to apply the diffraction methods in order to determine which structural changes occur by irradiation and pressure in different polymorphic modification of carbon (diamond, graphite, fullerene).

1. Diamond

As samples, we used natural-diamond powders with a mean particle size from 14–20 μm to 0.5 mm that was irradiated in a beryllium block of an MR reactor up to a fluence of 1.5×10^{21} (175 days in a neutron flux of about $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ with energies higher than 0.18 MeV). The samples were cooled in running water. The irradiated powders turned out to be strongly density inhomogeneous and were divided into ten fractions in Clerici solution with distilled water in the density range from 3.24 to 2.05 g/cm^3 (with an accuracy of no worse than 2%) [10]. Diffraction experiments were carried out with the diffractometer DISK [11] at the 4.5-MW IR-8 reactor. The wavelength of monochromatic neutrons was equal to 1.667 Å. Samples of various fractions with masses 50–100 mg were investigated [12].

According to the results presented in Fig. 1, as density decreases, the diffraction lines of diamond are broadened, the “tails” of diffraction lines overlap, and a “halo” corresponding to the formation of a fine-crystalline (“amorphous”)

material of the diamond-like type is formed. With a further decrease in density, the diffraction pattern exhibits a new halo, whose intensity increases gradually and whose position corresponds to the position of the first maximum on the pattern of irradiated graphite [13] or amorphous carbon (activated charcoal) (Fig. 2a). The absence of small-angle scattering (for $q > 2 \cdot 10^{-2}$) from all samples indicates that they are homogeneous in scales of 2–3 nm. The results can be treated as evidence of a polyamorphic transition from diamond-like to graphite-like glass, which occurs when density decreases and which is likely associated with a decrease in the number of nearest neighbors in the first coordination sphere from four to three (in contrast to its increase at high pressures).

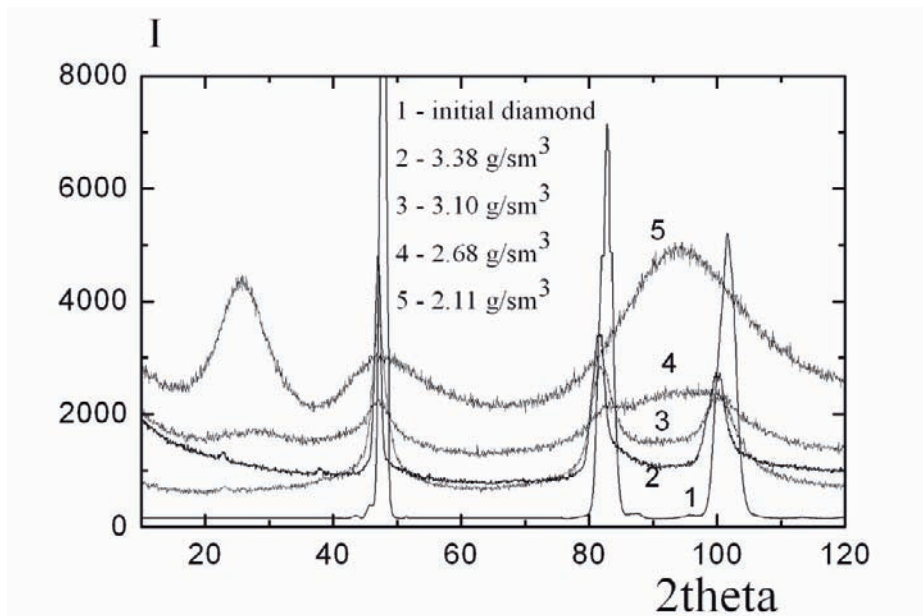


Figure 1. Diffraction patterns upon the transition from a diamond-like glass to a graphite-like structure upon change in density.

This transition is accompanied by a change in the resistivity of powders, which is measured by means of pressure contacts (Fig. 2b). The total change in resistivity is equal to six orders of magnitude in the density range under investigation and corresponds to a transition from the dielectric state to the metal one. The critical density, i.e., the density at which the transition occurs, is equal to $\rho \cong 2.7\text{--}2.9 \text{ g/cm}^3$ according both to diffraction measurements and to electric-resistivity measurements.

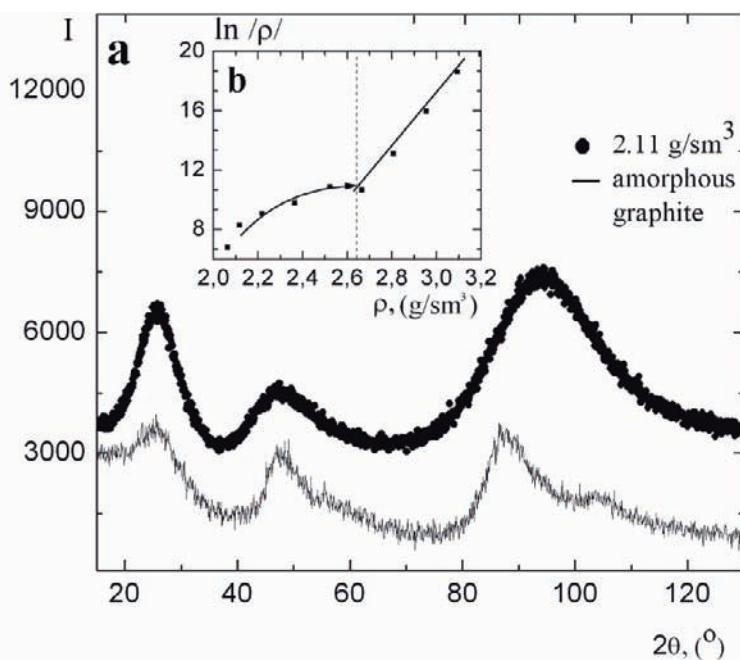


Figure 2. (a) Diffraction patterns for low-density irradiated diamond (2.11 g/cm^3) and amorphous graphite and (b) resistivity vs. density.

Since the polyamorphic transition occurs between disordered phases at low temperatures, the role of entropy is not as large as in polymorphic transitions in a crystalline state, and the transition occurs due to a change of the internal energy, as it is shown schematically in Fig. 3. According to Fig. 3, the transition between amorphous phases (diamond-like and graphite-like) is attributed to the existence of their crystalline analogs, which differ both in density and in the coordination number, so that polyamorphism is closely associated with polymorphism and the critical density of the transition corresponds to a saddle point and is approximately equal to the average density of crystalline analogues. A similar phenomenon likely occurs in high-pressure amorphous phases (SiO_2 , H_2O , etc.).

Stability of the graphite-like phase which appears in the irradiated diamonds as a result of polyamorphic transition with high decrease of density was studied using neutron and x-ray methods. The graphite-like structure was shown to be stable up to 50 kbar from ambient temperature to 1500 K at normal pressure. Simultaneously at rapid heating to 900–1000 K new (apparently metastable) modifications of carbon are formed. The diffraction patterns of the modifications do not coincide with those of known structures of carbon (diamond, lonsdaleite, graphite, chaoite, carbene, fullerene and its derivatives etc). It was shown that density of these structures does not differ much from the density of graphite, and at least one of these phases corresponds to a superstructure based on the bcc modification of C_8 with modified density [14].

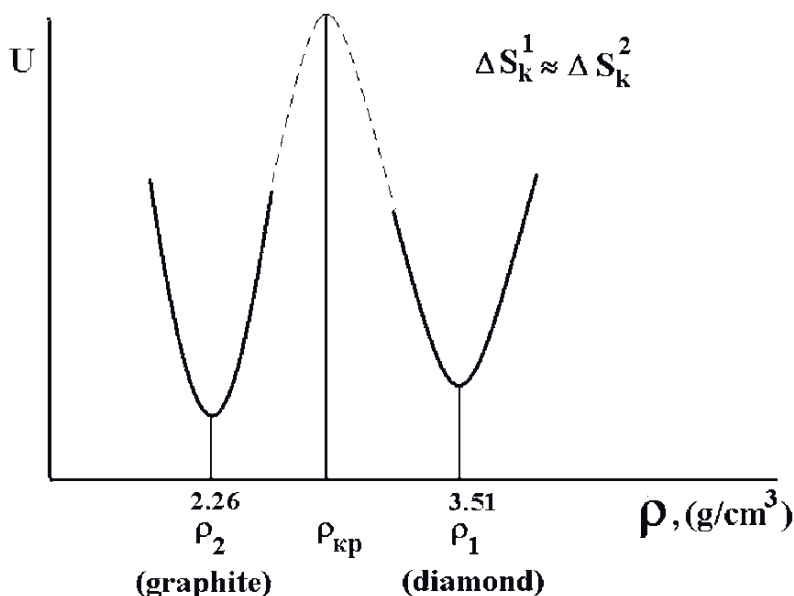


Figure 3. Internal energy U vs. density for a polymorphic transition at $\rho_{cr} \approx 2.7 \text{ g/cm}^3$; ΔS_k is the configuration entropy.

2. Graphite

Structural behaviour of graphite after the reactor irradiation with high fluence was studied by neutron diffraction. Samples of reactor graphite irradiated up to fluence 1.51×10^{22} were used. Dependence of the lattice spacings ratio c/a on fluence and temperature was established. The c/a ratio appeared to grow with the value of fluence and descends with the growth of temperature. At the temperature above 500°C the c/a ratio does not depend on fluence and corresponds to the initial value indicating the radiation annealing of defects.

As a result of comparison of the structural data after irradiation and under high pressure the dependence of c/a ratio on a volume change was deduced (Fig. 4). It was found that at the 3% volume change an amorphous phase appears in the structure of graphite. Graphite becomes completely amorphous at the relative volume change of 8%. Under high pressure the phase transition to lonsdeylite takes place at the relative volume change of 15%. Critical values of c/a , which indicate the structural instability of graphite, were determined. Under the irradiation the critical value of $c/a=3.10$ (an increase by 13%), under pressure $c/a=2.37$ (a decrease by 14%). So the graphite lattice loses stability at the same values of c/a regardless the sign of the volume change.

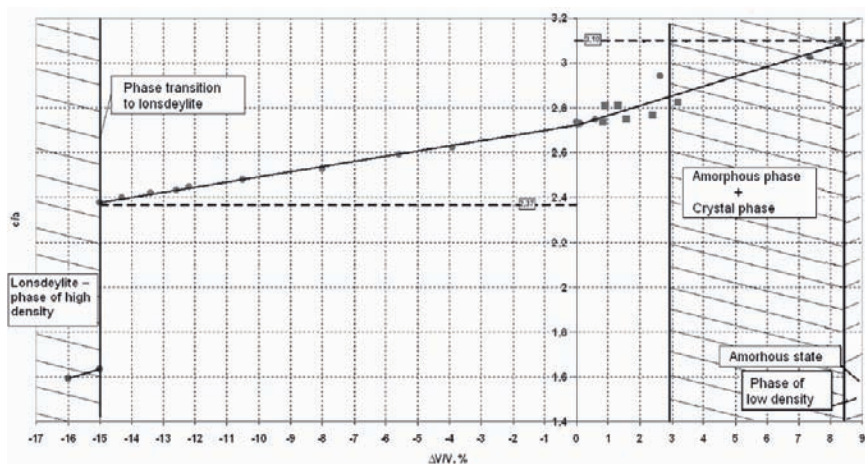


Figure 4. Change c/a relation in graphite with volume under pressure and irradiation.

In [15,16] it was shown that the pressure effect, resulting in a contraction of interlayer distances, gives rise to a monotonous hardening of the measured frequencies. An investigated longitudinal acoustic branch does not change its sinusoidal shape under pressure while the continuous evolution from quasi-two-dimensional to three-dimensional behavior was found for a transverse acoustic branch. It was pointed out that the observed higher rate of pressure variations of the lattice dynamics parameters as compared to the structural anisotropy can reflect changes of the crystal potential in graphite related to an available high pressure phase transformation from the layered to more isotropic lattice of lonsdeylite.

We can assume that the radiation amorphization of graphite is conditioned by softening (or decreasing to zero) of the phonon frequencies at the volume increase during irradiation. The increasing of volume is equivalent of negative pressure ~ 30 - 40 kbar (Fig. 5). Estimations show that in this case the amorphization is required to take place $\Delta V/V \sim 5$ - 6% according to a experiment. Therefore knowing graphite behaviour at high pressure ($\Delta V < 0$), it is possible to predict its behaviour at radiation ($\Delta V > 0$) and vice versa.

3. Fullerene

The investigation of the behaviour of fullerene under high pressures is important to determine the type of the intermolecular interaction and the type of possible phase transitions under a change of the volume. For this purpose the investigation of C_{60} and $C_{60}F_{48}$ [17] and $C_{60}D_{36}$ by neutron diffraction was carried out in the pressure range up to ~ 40 kbar by sapphire anvil technique [18]. The intensities of diffraction peaks do not change essentially for all C_{60} , $C_{60}F_{48}$ and $C_{60}D_{36}$ when the pressure increases. That points to the invariance of the structure type in this pressure range. At the same time the peaks shift towards large scattering angles in conformity with decrease of lattice spacing and unit cell volumes as the pressure increase.

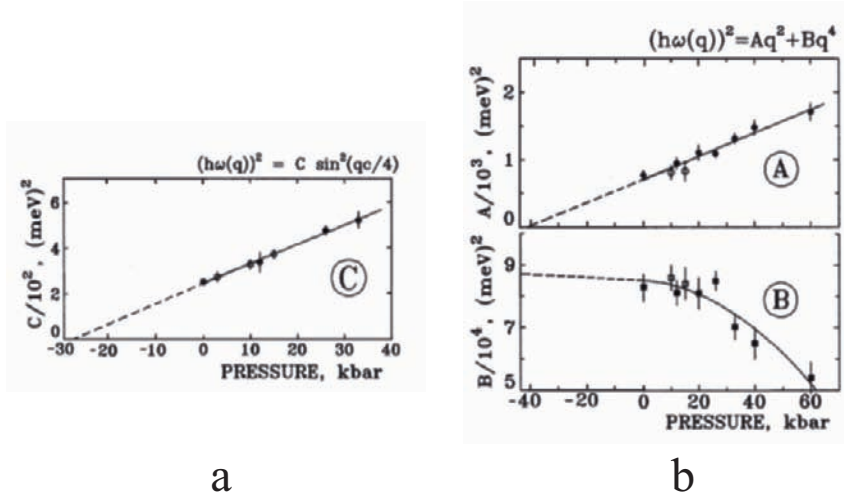


Figure 5. Pressure dependence of parameter C in the dispersion law for the LA-LO phonon branch (a) and pressure dependence of parameters A and B in the dispersion law for the TA_1 phonon branch (b).

The magnitudes of the relative change of the volume determined from the data of the change of the volume with the pressure in $C_{60}F_{48}$ and $C_{60}D_{36}$ show that the equation of state for both C_{60} and $C_{60}F_{48}$ compounds almost coincide within the experimental error. Thus, the main result is that the compressibilities of C_{60} and $C_{60}F_{48}$ in the studied pressure range are similar or close in spite of the large difference in the specific volumes and the presence of the additional fluorine shell in the $C_{60}F_{48}$ molecule. This similarity is absent in $C_{60}D_{36}$.

The explanation of compressibility follows, apparently, from the features of the intermolecular interaction. If one uses the potential (6-exp) [19], i.e., the sum of dipole-dipole attraction and the exponential repulsion, and connects the parameters of this potential with the equilibrium distance r_0 and the depth of the potential well ε , we have

$$K = \varepsilon/(r_0^2) - [6\alpha r_0(1/\alpha r_0 - 6) - 1], \quad (1)$$

for the second derivative value of the potential at the minimum point (or the elastic modulus K), where α is the factor of the exponential repulsion. Taking into account that the values of αr_0 are close for many molecular crystals and differ from the average value by no more than 10-15% [19] we can suppose that the expression in square brackets is constant. Then the quantity K will only depend on the correlation between the width and depth of the potential well ε/r_0^2 . Using the values of intermolecular radii of carbon ($R_C = 1.80 \text{ \AA}$) for C_{60} , fluorine ($R_F = 1.50 \text{ \AA}$) and hydrogen ($R_H = 1.17 \text{ \AA}$) [20] to estimate r_0 and the values of the active evaporation temperature $T_e \cong 830 \text{ K}$, 550 K and 700 K for C_{60} , $C_{60}F_{48}$, $C_{60}D_{36}$ respectively to estimate ε , we arrive at the conclusion that the values of $\varepsilon/r_0^2 \approx T_e/R^2$ are close for C_{60} and $C_{60}F_{48}$ and different for C_{60} and $C_{60}D_{36}$.

Consequently, the values of K and the compressibility should also be close. It means that the decrease of the potential well depth of the intermolecular interaction in $C_{60}F_{48}$ as compared to C_{60} is compensated by the decrease of the equilibrium distance r_0 . The qualitative conclusion about the decrease of the well width in $C_{60}F_{48}$ can be obtained from the analysis of direct structure data. The practically complete coincidence of the compressibility module and equations of state for C_{60} and $C_{60}F_{48}$ established demonstrates the similarity of potential wells for intermolecular interaction in these compounds at least near the well bottom. K for $C_{60}D_{36}$ is higher for smallest intermolecular radii R_H .

Pure fullerenes and fullerenes with hydrogen irradiated in a nuclear reactor at the fluence up to 10^{19} were investigated. It was shown that at such fluences the complete irradiation glass-formation comes and one can see the well-defined "gallo" on neutron diffraction patterns. The obtained results show that hydrogen saturation decreases the fullerene crystal lattice stability against irradiation. At annealing of the irradiated samples up to 350°C the wide "gallos" gradually disappear and instead new "gallos" come into existence at different scattering angles. The pattern do not essentially vary with anneal time increasing from 6 to 100 hours at the highest temperature. The obtained results point to the occurrence of the different type of the amorphous structure.

The other method of amorphous fullerenes production –the ball milling amorphisation – was investigated. Samples of amorphous fullerenes were produced by application of the mechano-activation treatment (milling in a ball mill) and their structure (Fig. 6) and sorption properties were investigated.

By neutron diffraction method it was observed that amorphization comes after milling during two days (Fig. 7). Doing so sorption of hydrocarbons (geptan and others) and hydrogen abruptly increases in comparison with a crystal powder. Structure stability of amorphous fullerenes against temperature and pressure action was studied. It was established that in amorphous fullerenes at temperature increasing up to 400°C narrowing and increasing of fullerene "gallos" occur, corresponding to gradual restoring to a crystal structure of the initial fullerene. But at further temperature increasing the first "gallos" decrease and disappear at 1000°C while the "gallos" at great scattering angles remain. A detectable low-angle scattering appears at a time. The similar behaviour take place also in equimolecular mixtures of the fullerenes (C_{60} - C_{70}). The obtained results can be treated as a polymorphic transition from a molecular (fullerene) glass to a atomic (diamond-like) or polymer glass.

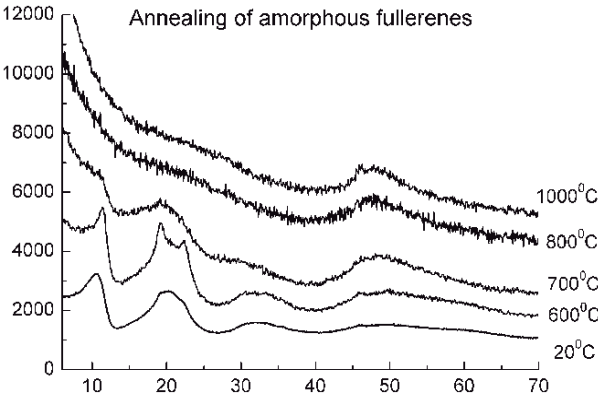
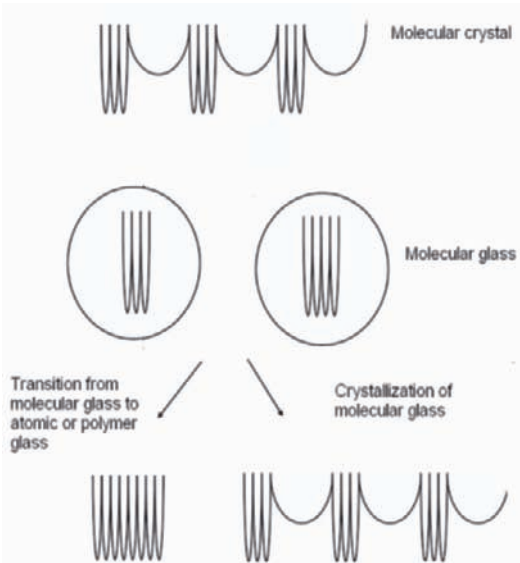


Figure 6. Polyamorphic transition in amorphic fullerenes.

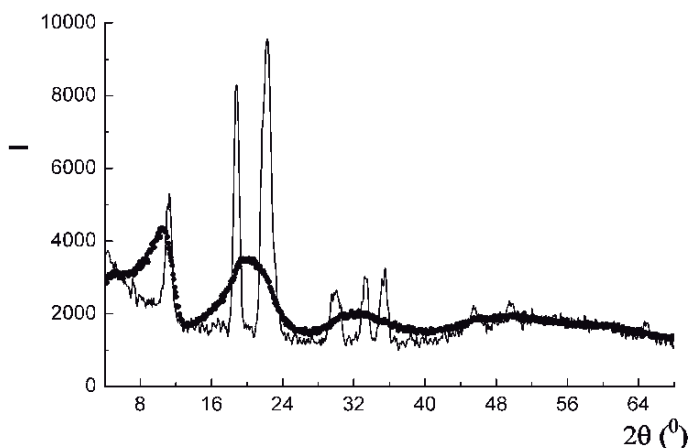


Figure 7. Neutron diffraction pattern of ball-milling amorphous C_{60} (—) and polycrystal C_{60} (•).

4. Conclusions

Thus obtained results show that the polyamorphic transitions occur not only at compression (SiO_2 , H_2O , etc.) but at extension as well (C) in the systems having stable or metastable crystal analogs with a different density and a different coordination number z . At the minimal $z=2$ (chain structures) the transitions may occurs only at compression, at the maximal $z=12$ (close-packed structures) - only at extension, at the intermediate z ($2 < z < 12$) - in the both cases. At the transitions structure-sensitive properties change and new metastable phases can appear. Amorphization under radiation (crystal lattice extension) can be associated with a softening of phonon frequencies. The transitions in the molecular glasses consisted from the molecules with unsaturated bonds are accompanied by creation of atomic or polymeric amorphous systems.

Acknowledgements

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ON SOME SPECIAL FEATURES OF CARBON NANOSTRUCTURE FABRICATION IN ARGON ARC DISCHARGE

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Abstract. We report on the investigation of some carbon structures fabrication in the discharge arc. The formation of a cathode deposit in the form of a cylinder at all the used argon pressures is usually observed. It is shown that the ledge-deposit mostly has been consisted of the spherical particles coagulating in the form of filaments. The X-ray diffraction of a ledge-deposit showed only the characteristic peaks of hexagonal graphite. A metallic foil being put in the discharge chamber is covered with some colourless thin needle-like plates. The X-ray diffraction of these plates showed the peaks of hexagonal α - carbine.

Keywords: arc discharge, argon, cathode deposition, fullerene, X-ray diffraction, graphite, needle-like plate, hexagonal α - carbine

1. Introduction

The most widely used method of fullerene and carbon nanotube preparation is an arc discharge in a buffer gas. Helium is usually applied as the gas. Argon is more widespread and cheap gas than helium. However the fullerene yield is less than 2 % with that gas whereas in a helium arc discharge it is about ten times greater. We have worked out an effective method of small quantity fullerene preparation by means of an argon arc discharge [1-3]. This report informs about the further investigation in this direction.

2. Experimental

The experimental installation consists of a vacuum bell jar, a water-cooled cylindrical discharge chamber, an inlet gas system and a rectified 60 V source. A graphite rod with a diameter 6 mm is used as an anode. A graphite plate with dimensions 30×15×5 mm is used as a cathode. The electrodes are arranged horizontally at the end faces of the discharge chamber. A cathode can be moved along its axis. The chamber is placed inside the vacuum bell jar. An initiation and a burning of an arc can be controlled through the peepholes in the bell jar. This bell jar is preliminary evacuated to the residual pressure of $p = 1$ Pa with a backing pump. Then all the working volume is filled with argon.

Resistive heating of electrodes during their brief contacting initiated an arc. The interelectrode gap in the operating mode is varied in the range 0,1...5 mm. The arc

current is varied from 30 to 150 A, and the argon pressure - from $1 \cdot 10^4$ to $7 \cdot 10^4$ Pa. The arc discharge burning time was about 30 min.

After cooling the electrodes and inletting an air in the bell jar, a soot is removed from the chamber walls, weighed on an analytic balance and filled with toluene. After storing the soot in toluene for several days, we measured the transmission spectrum of the mixture with a SF-26 spectrophotometer. Then the colored mixture is poured out, the residual toluene is evaporated at the temperature $T = 500$ K from the soot and it is weighed once again. The relative content of fullerenes in the soot is measured from these data [2,3].

X-ray diffraction analysis of the samples is performed on a DRON-4 apparatus with Cr K_α radiation. As a monohromator, we applied a crystal of pyrolytic graphite. The carbon structure morphology is investigated with a REM-200 electron microscope. The infrared spectra of the optical transmission of the pressed sample tablet in KBr are measured on a Specord M80 spectrophotometer.

3. Results and Discussion

In the argon arc we observed visually the formation of the cathode deposit in the form of a cylinder at all the used gas pressure. The ledge of such form has grown on the cathode surface exactly opposite the anode and its diameter was nearly equal to the anode profile. In the majority of cases, a regime was spontaneously established at which an increment of the deposit height was not accompanied by an electrode locking.

The average growth rate of this formation was in the range from 1 to 4 mm/min and it strongly depended upon a discharge current and a gas pressure. The average specific weight of a ledge, measured by dividing its mass to geometric volume, was about $1,3 \cdot 10^3$ kg/m³. This value nearly coincides with a weight of the cathode deposit obtained in the helium discharge arc [4]. Maximum length of the grown cylinder was 65 mm.

Figure 1 illustrates the general view and internal structure of the ledge. It shows the micrographs of a ledge-deposit fracture at various magnification degrees. From Figure 1,a it is seen that the inner part of the formation is a rather friable structure mostly consisting of the thin ($\sim 0,05$ mm diameter) carbon filaments. All these filaments (fibers), on the whole, are directed along the symmetry axis of a ledge (Fig. 1,b) and at a greater magnification they seem to be consisting of the coagulating spherical formations.

The outer surface of the ledge-deposit is been formed by the peculiar ring-like carbon structures (Fig. 1,c). They also consist of the fine coagulating spherical specimens, which in turn, consist of the even smaller coagulating objects. The external surface of the ledge is rather rough (Fig. 1,a). We suppose such structures posses a very large effective surface area; therefore, they could serve as a perspective material for the hydrogen accumulation.

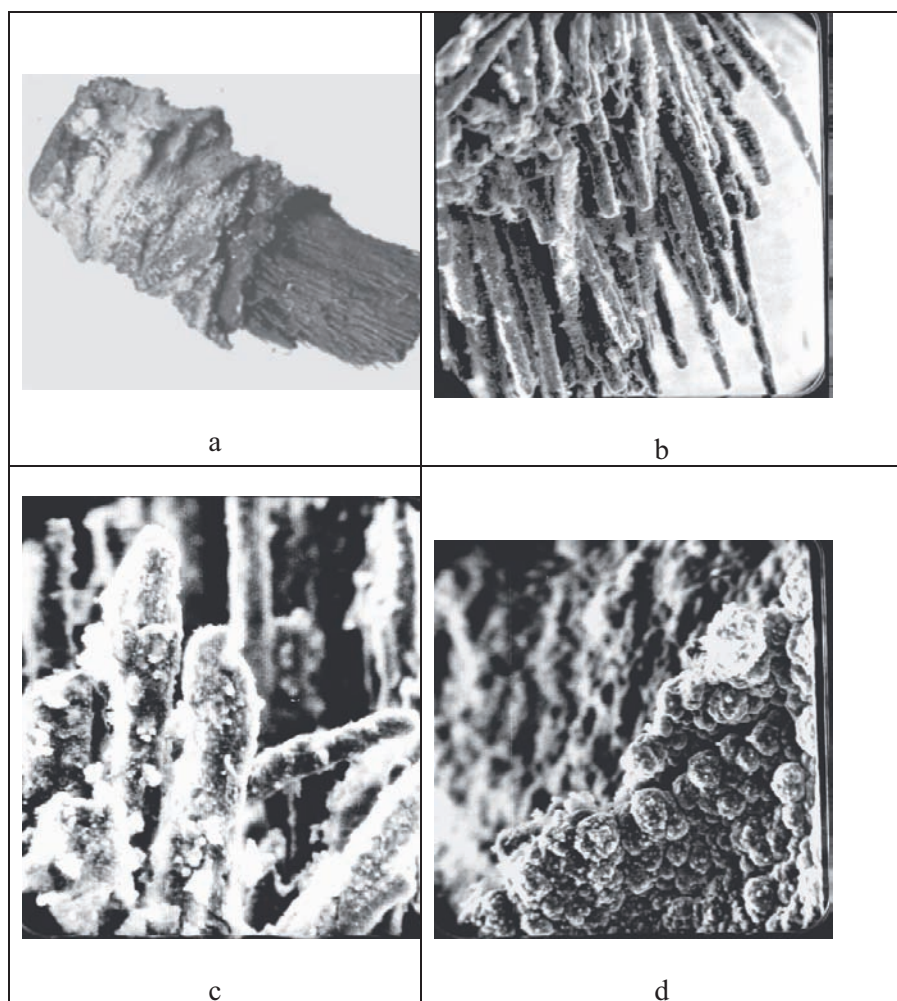


Figure 1. Photograph (a) and electron micrograph (b, c, d) of a ledge-deposit fracture: a - $\times 5$, b - $\times 75$, c - $\times 225$, d - $\times 150$.

We have performed X-ray diffraction investigation of the ledges obtained in various regimes of the arc. The X-ray peaks of hexagonal graphite have been only observed in all diffractions. It follows that the spherical particles observed in Fig. 1 mainly consist of graphite.

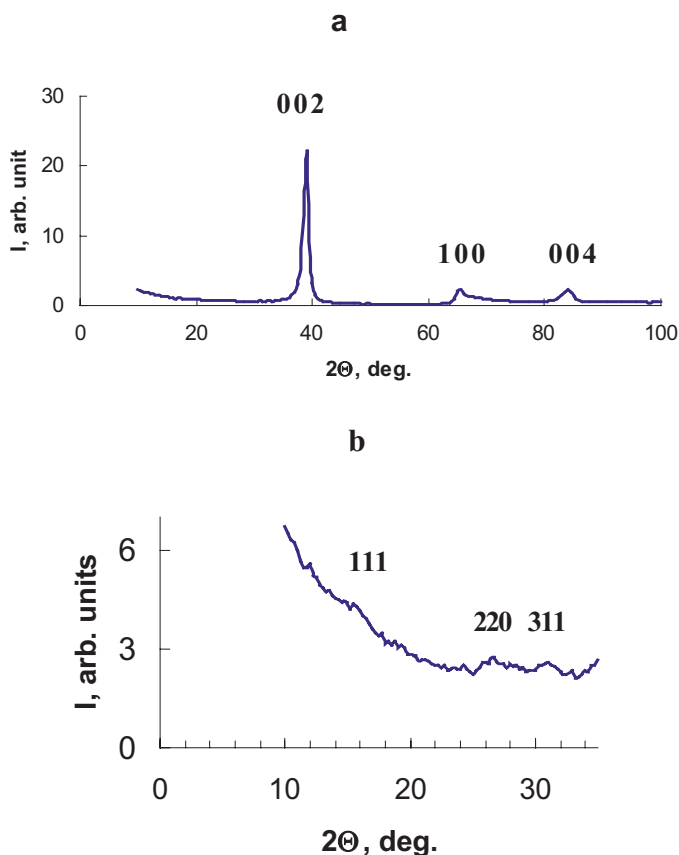


Figure 2. X-ray diffractions of the cathode deposits: a - specimen 1, b – specimen 2.

In Fig. 2,a a typical X-ray diffraction pattern for one of the ledge-deposit is shown. One can see the characteristic X-ray peaks of hexagonal graphite.

Also, in some cases the small maxima have been registered at the region of the small angles in the X-ray diffractions of the ledge-deposit. The part of such X-ray diffraction in the angle region $2\Theta = 10 \dots 35^\circ$ is shown in the Figure 2,b, where the mentioned maxima are clearly distinguished. Their positions coincides with the (111), (220) and (311) X-ray peaks of the FCC – structure of fullerite. Consequently, in the process of an argon arc burning there is a possibility of the most stable fullerene molecule formation in the process of carbon atom moving across the plasma into the cathode deposit.

Some of the grown ledges were used as an anode for the second sputtering in an arc. In this case it was found that the relative fullerene content in the soot was more higher than that is the case of graphite utilization [2]. Subsequent investigation has shown that the effect takes place only if the ledge-deposit is kept in an inert atmosphere. Practically, its any exposition of the samples in atmosphere air lead to a decrease of the fullerene yield. We suppose that such a passivation is caused by a

sorption of oxygen atoms on the surface and in volume. Under the high temperature conditions, these atoms desorb and have negative effect on the formation of the fullerene-like structures in the arc plasma [5].

In the work, we have performed complex X-ray structural investigation of dispersed products deposited on various details within the discharge chamber. The investigation is accompanied by measurement of the relative fullerene content in the soot by means of the weighing method [2,3] and an optical density of toluene infusion. In all the cases, the existence of fullerenes in the infusion is accompanied by an appearance of an enormous halo in the angle range $2\Theta = 15...35^\circ$ in the X-ray diffraction. Moreover, the height of this halo increases with increasing fullerene content in the soot and with increasing optical density of the infusion.

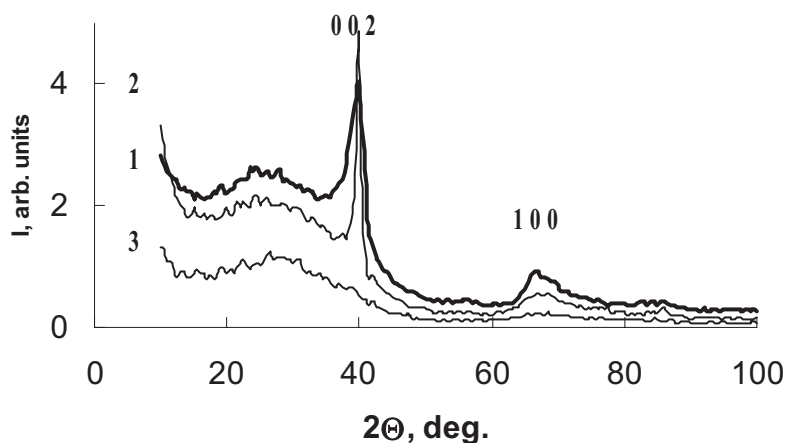


Figure 3. X-ray diffractions the soots: 1 – on the walls of the discharge chamber, 2 – on the cathode surface, 3 – on the anode holder surface.

Figure 3 shows the X-ray diffraction of the soot deposited on the walls of the discharge chamber (curve 1), on the cathode surface (curve 2) and on the anode holder surface (curve 3). In all the curves, one can see the amorphous halo at the angle range $2\Theta = 15...40^\circ$ and the characteristic graphite reflexes. On a background of the halo, there are the weak peaks, the most part of which coincides with the most intensive peaks of the FCC-structure of fullerite C_{60} . However, the (002) and (100) peaks of graphite are seen only in the curves 1 and 2. This fact indicates that the positive anode potential prevents formation of the graphite structure and, perhaps, it contributes to binding of the atoms (or the atomic complex) in the fullerene-like structures. Moreover, it should be emphasized that only the toluene tincture of the soot collected from the water-cooling walls of the chamber has shown the characteristic (for the C_{60} and C_{70} fullerene molecules) red-brown color. In other words, in spite of the tremendous halo existence in the X-ray diffraction showing the presence in the soot some fullerene-like structure, the spectrophotometric investigation of an infusion of this soot does not corroborate an

existence of C_{60} , C_{70} molecules. In our opinion, these data testify the formation of a toluene insoluble chemical compound of fullerene molecules on the electrode's surfaces at high temperature. The intensive thermal treatment obviously leads to the molecule polymerization due to the covalence bonds. Because of these strong bonds, the molecules should be incapable to dissolve in toluene.

The fulleren-containing (colored) toluene infusion of dispersing products was separated from the insoluble sediment and put into a glass evaporating cell equipped with a water-cooling device for the cooling of vapor. Evaporating and recondensing of pure toluene was performed at the temperature $T = 500$ K.

The X-ray diffraction of the obtained extract is given in Fig. 4. The FCC-lattice reflexes of fullerite C_{60} are identified in this diffraction.

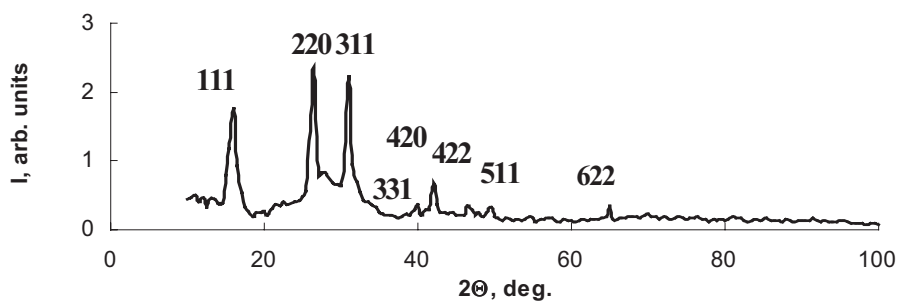


Figure 4. X-ray diffraction of extract.

Figure 5 shows an infrared spectrum of this extract. Almost all the peaks observed in this spectrum correspond to the crystal C_{60} .

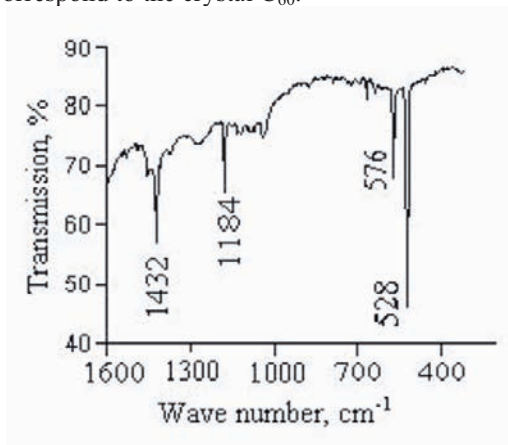


Figure 5. Infrared spectrum of extract.

In our investigation, we noticed that a metallic foil surface, being put near one of the ends of the discharge chamber, was covered with some flat uncolored ledges. At more attentive examination these ledges prove to be thin, flexible, needle-like plates growing densely perpendicular to a foil.

These needle-like plates are easy to separate from the substrate and also easy they to be mechanically split into more subtitle long objects. With an optical microscope, it is observed that the tip of these objects can reflect the incident light and expand it into a spectrum.

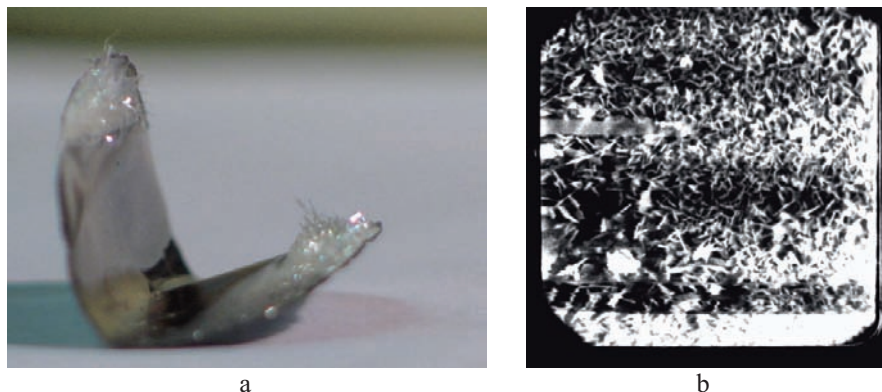


Figure 6. Photograph of the nickel foil with some needle-like plates (a) and its micrograph (b): a - $\times 4$, b - $\times 270$.

Figure 7 shows a photograph of the nickel foil with some needle-like plates (a) and electron micrograph of their surface (b) in the region of their formation. One can see that these plates are mostly concentrated in two regions of the foil surface, which are situated at higher temperature than the rest of the foil. Most of the needles fall down during the process of installation, and thus they are not seen in Fig. 7,b. The interesting feature of Figure 7,b is an existence of the fine crystals in the region of the falling needles. Presumably, these crystals have some carbon structure.

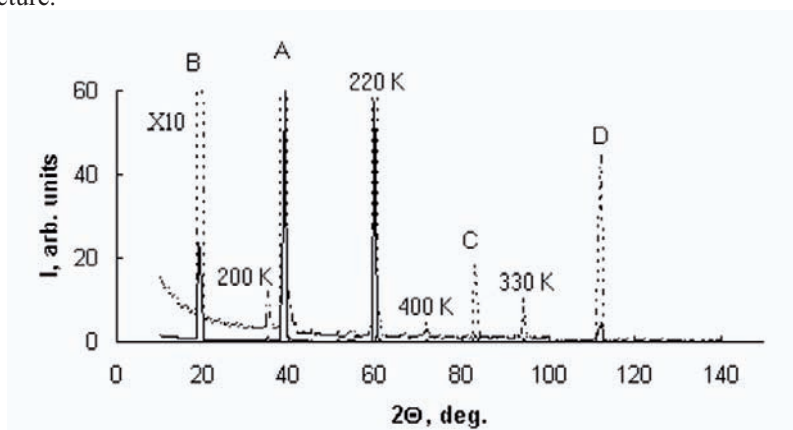


Figure 7. X-ray diffraction of the needle-like plates (the dashed line is the diffraction increasing at 10 times).

X-ray diffraction of the needle-like plates is given in Figure 8 where one can see several narrow reflexes of various heights. We could not identify these reflexes completely, and these reflections seem to be of different nature. The locations of four of these maxima coincide with (200), (220), (400) and (330) reflexes of hexagonal α -carbide [5]. The peak A, situated at the angle $2\Theta = 40^\circ$, corresponds to the typical graphite interplanar distance $d_0 = 0,34$ nm. The peaks B and C correspond to the interplanar distances which are multiple to the distance d_0 ; hence these peaks could correspond to various orders of X-ray diffraction from this d_0 . The peak D situated at the angle $2\Theta = 115^\circ$ could be attributed to the reflex (203) of hexagonal α -quartz SiO_2 [5]. On the other hand the peak A may be corresponds to the reflex (101) of this compound too. Origin of this chemical mixture could be some admixtures existing in used electrodes.

It should be noted that the appearance of the observed objects is similar, to some degree, to the carbon nanotube cobweb obtained by ablation of graphite [6].

4. Conclusions

- (1) The conditions of formation of a deposit on a cathode in the form of the long cylinder are determined.
- (2) It is found that this deposit consists of spherical particles, which are characterized by the structure of hexagonal graphite.
- (3) It is shown that the toluene insoluble fulleren-like structures may form in the discharge chamber.
- (4) The conditions of the appearing of thin uncolored plates in the chamber are determined.
- (5) The X-ray diffraction of these objects shows their great degree of crystallinity.

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POSITRON SPECTROSCOPY OF LIQUID CRYSTALLINE ORGANIC MATERIALS CONTAINING C₆₀ FULLERENES

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Abstract. Free-volume structure in the lanthanum salt of laurinic acid in crystalline and liquid-crystalline states and an effect of dissolved C₆₀ molecules on the mean nanovoid radius and concentration were studied by means of the positron annihilation technique. La(C₁₂H₂₅COO)₃ clathrate compound with dissolved C₆₀ molecules was obtained, which is thermodynamically more stable than a simple mixture of components. Increased mean nanovoid radius (from 0.28 to 0.39 nm) after the inclusion of C₆₀ molecules and concomitant decrease of the positronium annihilation rate by a factor of 2.7 indicate the decrease of the smallest nanovoid concentration.

Keywords: fullerenes, nanovoid, positronium, liquid crystal, lanthanum laurate

1. Introduction

Lanthanum laurate La(C₁₂H₂₅COO)₃ exemplifies ionic metal mesogenes, which are known to form thermotropic and lyotropic liquid crystals [1]. Anisotropy and high molecular mobility are essential properties of liquid crystals, which ensure the fast rate of information processing systems on their base. Molecular mobility is also known to depend on the presence of the free-volume defects. These are intermolecular cavities (nanovoids) or atomic-size vacancies.

Lanthanum laurates in crystalline (powder) and liquid-crystalline states, as well as after dissolution of C₆₀ fullerenes were studied by means of the positron annihilation technique which is extremely sensitive to the free-volume defects.

Lanthanum laurates were prepared as in Ref. [2]. The spectra of the angular correlation of annihilation photons (ACAP) were measured in a standard long-slit geometry using ²²Na radioactive isotope as a positron source.

2. Experimental

Positronium (Ps) annihilation probability in the nanovoids of the samples in initial state is found to be 11.13 %, whereas the mean nanovoid radii for the crystalline and liquid-crystalline samples are 0.33 and 0.28 nm, respectively. After dissolution of C₆₀ fullerenes probability of Ps annihilation in nanovoids is decreased by the factor of 2.7. The general spectrum of lanthanum laurate initial pattern is presented in the Fig. 1. The calculated parameters of the investigated patterns are resulted in the Table 1.

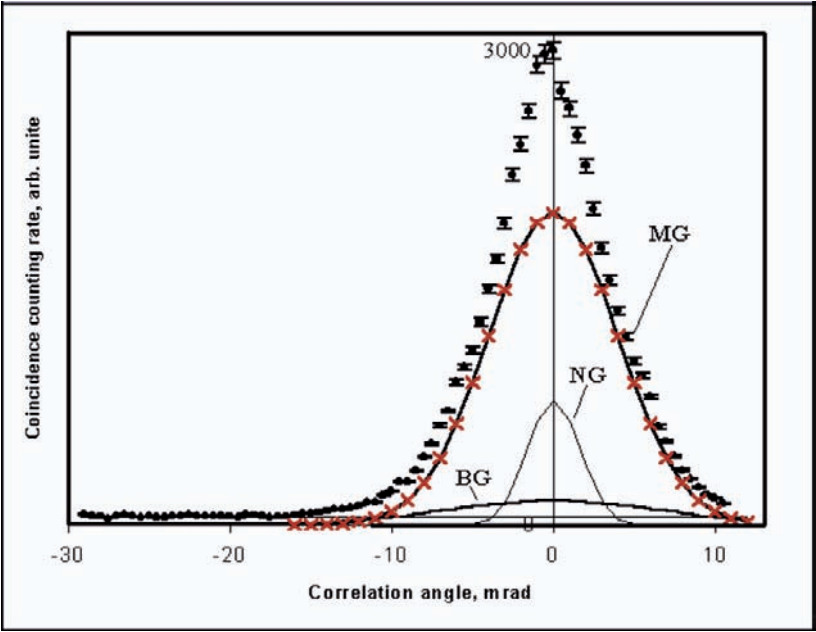


Figure 1. Lanthanum laurate angle correlation of annihilation photons spectra in slowly cooled from melted state (●) and it's expansion to narrow (NG), mean (MG) and broad (BG) Gaussians.

TABLE 1. Parameters of ACAP spectra and the calculated sizes of nanovoids in lanthanum laurate patterns

pattern state	crystalline powder	slowly cooled from melted state	with C ₆₀ fullerenes	C ₆₀ fullerite*
Mean nanovoid radius, nm	0,325	0,279	0,390	-
narrow Gaussian intensity S _N , %	11,13	12,65	4,70	-
mean Gaussian intensity S _N , %	77,57	77,11	87,72	78,3
broad Gaussian	11,30	10,24	7,58	21,7

intensity $S_N, \%$				
r_M	0,1193	0,1182	0,1160	0,121
r_B	0,0688	0,0714	0,0440	0,0410

* Values of parameters are taken from [3]

At the same time the mean nanovoid radius, sampled by Ps, increases to 0.39 nm (Fig. 2). This is an evidence that annihilation in small nanovoids is strongly suppressed. Observed changes are accompanied by the increase in the positron annihilation probability on oxygen anions from 77.3 to 87.7 % and the decrease in their radius from 0.160 ($\pm 0,001$) to 0.156 nm.

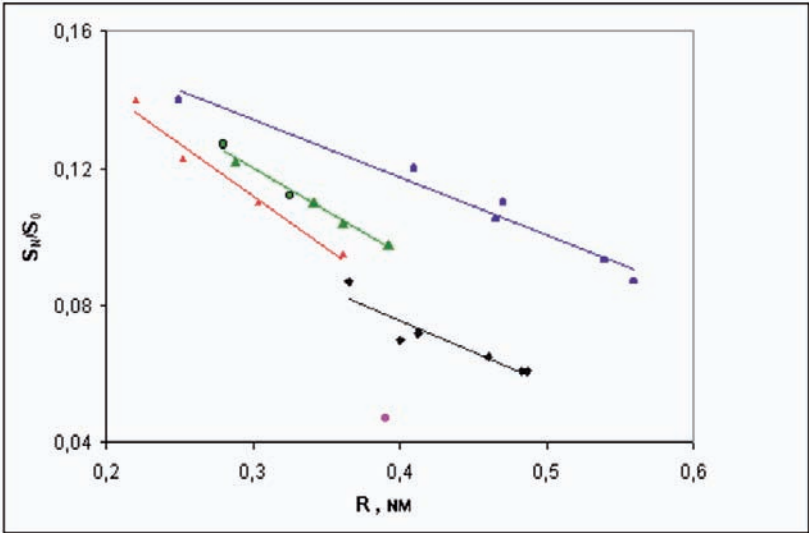


Figure 2. Intensity dependence of narrow ACAP spectra's component (S_N) from nanovoid radius (R) for first fraction of tri-glucerids in crystalline state at 22 °C (◆) and 36 °C, the sixth fraction of tri-glucerids in liquid state (▲), the mix of first and sixth fractions at 25 °C (Δ) for two patterns $\text{La}(\text{C}_{12}\text{H}_{25}\text{COO})_3$ (●) and with fullerenes (■) at 22 °C.

The van der Waals bonds between carbon atoms in C_{60} fullerene molecule and the outer nanovoid surface ensures the decrease in the surface energy and increases thermodynamic stability of resulting clathrate. Taking into account that the van der Waals bond energy between carbon layers is in the range of 0.44 – 0.88 eV, the inclusion of single molecule into organic matrix results in the decrease of the system's free energy by about 40 eV per C_{60} molecule. Isolated in the matrix C_{60} fullerene is supposed to form solvate cover with neighboring hydrocarbon radicals. Electrostatic potential on the surface of spherical fullerene-like cluster is a major factor that affects the ordering processes during hybrid nanostructure formation.

3. Conclusions

1. $\text{La}(\text{C}_{12}\text{H}_{25}\text{COO})_3$ clathrate compound with dissolved C_{60} molecules was obtained, which is thermodynamically more stable than a simple mixture of components.
2. Increased mean nanovoid radius (from 0.28 to 0.39 nm) after the inclusion of C_{60} molecules and concomitant decrease of the positronium annihilation rate by a factor of 2.7 indicate the decrease of the smallest nanovoid concentration [2].

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PROPERTIES OF PTFE – MWNT COMPOSITE MATERIALS

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Abstract. It is shown that reinforcement of PTFE by 15% of multiwall carbon nanotubes (MWNT) results in more than 2 times increase of strength parameters compared to starting PTFE matrix. Non-trivial temperature dependences of electrical resistance and thermal electromotive force were observed. Percolation threshold determined from dependence of the composite specific resistance on MWNT concentration was near 6% mass. Concentration and nature of oxygen-containing MWNT surface groups influence the strength parameters of the composite material.

Keywords: multiwall carbon nanotubes (MWNT), polytetrafluoroethylene (PTFE), surface groups, conventional yield strength, coefficient of elasticity

1. Introduction

Due to their unique mechanical and electronic properties carbon nanotubes (CNT) are promising for use as reinforcing elements in polymer matrixes [1, 2]. The main problems are creation of strong cohesion of CNT with a polymer matrix and uniform distribution of CNT in matrix [3]. The goals of this work were development of PTFE-MWNT nanocomposite material with high mechanical characteristics and investigation of influence of MWNT surface groups on mechanical and electronic parameters of the composite material.

2. Experimental

Multiwall carbon nanotubes (MWNT) were obtained according to the method described in [4, 5]. The structure of MWNT and PTFE-MWNT composites was studied with use of transmission electron microscope JEM-100CXII. Average diameter of nanotubes was 10-20 nm, surface area (determined by argon desorption method) – 250-400 m²/g, bulk density of MWNT powder 20-40 g/dm³. As-obtained MWNT were used which contained 6-20% of minerals (rests of metal oxide catalyst).

In order to elucidate how the composite material mechanical parameters depend on MWNT surface groups composition the samples of MWNT were subjected to anode oxidation (200 A.h/kg) in aqueous sulfuric acid. Oxidized product was washed with water to pH=6-7, dried and disintegrated. A part of this

oxidized material was subjected to thermal treatment 20 sec at 800°C. Surface area of the starting, oxidized and thermally treated MWNT was 240, 220, and 280 m²/g correspondingly.

The nature of MWNT surface was characterized by X-ray photoelectron spectroscopy method (XPS). XPS spectra were obtained with use of Kratos Analytical SERIES 800 XPS spectrometer with non-monochromatic MgK α (1253.6 eV) X-ray source. While recording XPS spectra vacuum in the analytical chamber was maintained at level of 10⁻⁹ Torr.

Content of oxygen in MWNT appeared to be considerably lower compared to carbon fibers [6] for all starting, oxidized and thermally treated samples of MWNT. Anode oxidation resulted in increase of relative phenol group concentration. After thermal treatment of oxidized material concentration of phenol groups decreased while relative concentration of carbonyl groups increased. The energy resolution defined as half-width of Ag3d_{5/2} band was 1.1 eV. Precision of bond energy determination was ≤ 0.1 eV. The bond energy E_b was calibrated by the standard C1s graphitic carbon electrons band, $E_b = 284.5$ eV. The analysis of XPS band profiles was performed with use of XPSPEAK 95 program (Version 2), which use mixed Gaussian-Lorentsian distribution function. The samples were studied in form of a compressed powder.

PTFE-MWNT composite materials were obtained with use of mixing of PTFE powder (F-4PN20) with MWNT in presence of surface active compounds; coagulation of aqueous PTFE dispersion F-4D with MWNT; hot pressing. Samples of composites containing 5, 10, 15 and 20% of MWNT were prepared. For these samples conventional yield strength $\sigma_{0.2}$, coefficient of elasticity E_c under single-axes compression, thermo-electromotive force, and electrical resistance were measured. Mechanical parameters were measured with use of 2167-R50 machine with automatic recording of deformation plot. Parameters $\sigma_{0.2}$ and E_c were calculated from the deformation plots by standard methods.

Thermo-electromotive force and specific electrical resistance were measured by the standard 4-electrode method.

Electron images of original and treated MWNT are shown in Fig. 1.

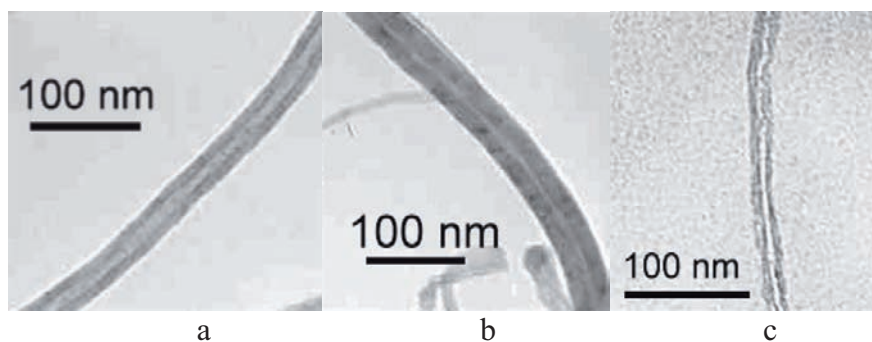


Figure 1. a - starting MWNT; b - after anode oxidation; c - after thermal treatment.

As is seen, anode oxidation in sulfuric acid does not corrupt the nanotube structure. After thermal treatment of the anode oxidized nanotubes substantial thinning and loosening of walls was observed.

It was observed substantial heterogeneity of MWNT distribution in the PTFE matrix (Fig. 2). The tubes form clusters loosely bonded with matrix.

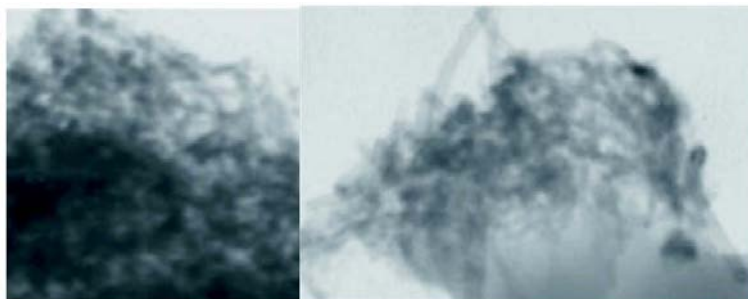


Figure 2. Thin sections of PTFE - MWNT(15%) composite.

Typical XPS spectra of MWNT are shown in Fig. 3.

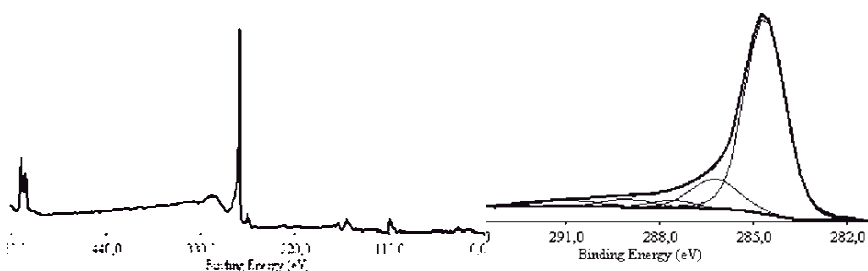


Figure 3. Typical XPS spectra of MWNT.

According to the XPS data content of oxygen in untreated MWNT, after anode oxidation, and after short-time thermal treatment in air MWNT was 0.6; 1.1; 2.3 atomic % correspondingly. This is significantly lower compared to carbon fibers both untreated and after similar treatment [6]. In Table 1 there are listed relative concentrations of oxygen-containing groups identified by bonding energy [6, 7].

As is seen (Table 1) anode oxidation leads to increase of relative concentration of phenolic and carbonyl groups and to decrease of carboxyle and carbonate groups concentration. After thermal treatment concentration of phenol and carbonate groups decreased while relative concentration of carbonyl and carboxyl groups increased.

Highest mechanical parameters were observed for composite samples containing 15% MWNT. Values of $\sigma_{0,2}$ and E_c for composite materials obtained by different methods, commercial PTFE-coke composite material F4K20, and pure PTFE are listed in Table 2. Substantial scattering of data was observed. Probably

this indicates that the composite samples obtained are not sufficiently homogeneous.

As is seen (Table 2) filling of PTFE matrix with MWNT increases both yield strength and elasticity coefficient of material.

TABLE 1. Relative concentrations of oxygen-containing groups in MWNT and corresponding bonding energies [6, 7]

MWNT sample	Relative concentration, atomic %			
	$E_b = 286.1-286.3$ eV Phenolic and alcohol	$E_b = 286.1-286.3$ eV Carbonyl, quinone	$E_b = 286.1-286.3$ eV Carboxyl, ether	$E_b = 286.1-286.3$ eV Carbonate and/or adsorbed CO, CO_2
Starting	49.1	17.2	17.2	16.5
After anode oxidation	53.8	19.8	13.6	12.8
After thermal treatment	51.1	23.4	15.3	10.2

TABLE 2. Mechanical parameters of PTFE, composite materials PTFE-MWNT and F4K20

Material/method	$\sigma_{0.2}$, MPa	E_c , MPa
Composite/mixing of MWNT and PTFE powders	13-18	700-1500
Composite/coagulation of PTFE aqueous dispersion on MWNT	16-24	800-1300
Pure PTFE	10.6	570
Commercial composite F4K20	11.5	685

In Fig. 4 there are shown compression plots for composite materials obtained by mixing of PTFE (F-4PN20) and MWNT powders with following hot pressing. The curves 1-3 corresponds to composites containing MWNT with different surface state, 4 – pure PTFE. In Table 3 there are listed conventional yield strength and coefficients of elasticity calculated from compression plots.

TABLE 3. Mechanical parameters of PTFE and composite materials PTFE-MWNT

Sample	Density, g/cm^3	$\sigma_{0.2}$, MPa	E_c , MPa
PTFE + starting MWNT	2.09	13.4	940
PTFE + electrochemically oxidized MWNT	2.0	16	560
PTFE + electrochemically oxidized and thermally treated MWNT	1.84	-	-
Pure PTFE	2.16	10.6	570

It is seen from Fig. 4 and Table 3 that introduction of starting MWNT into PTFE matrix increases both yield strength and elasticity coefficient of the material. Introduction of electrochemically oxidized MWNT resulted in increase of yield strength without noticeable change of elasticity coefficient.

At the same time electrochemically oxidized and thermally treated MWNT considerably change strength of the composite materials and mode of its deformation. The strength decreases while compression-deformation plot acquires S-like shape

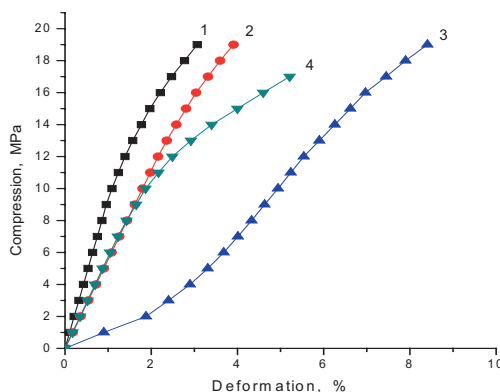


Figure 4. Compression-deformation plots for samples:

1 - composite PTFE-starting MWNT; 2 - composite PTFE-oxidized MWNT;
3 - composite PTFE-thermally treated (after oxidation) MWNT; 4 – pure PTFE.

which is characteristic for highly porous cellular polymer materials and porous graphites. It is difficult to determine yield strength and elasticity coefficient from such plot. Probably electrochemically oxidized and thermally treated MWNT reacts with PTFE matrix while hot pressing because of defective structure formed after thermal treatment of oxidized MWNT. This results in evolution of gas and formation of empty cavities around nanotubes. In this case nanotubes do not work as reinforcing elements.

The percolation threshold (θ_c) determined from concentration dependence of electrical resistance was near 6% mass MWNT.

In Fig. 5 there are shown typical temperature dependences of electrical resistance and thermo-electromotive force for composite containing 20% MWNT in PTFE matrix. Heating of PTFE-MWNT composite samples from room temperature to 325°C does not result in noticeable change of specific electrical resistance (ρ). At that differential (compared to copper) thermoelectromotive force (E_T) strongly increases. After cooling value of ρ increases nearly 3 times, temperature coefficient of electrical resistance (TCR) becomes negative, some change is observed in character of $E_T(T)$ dependence plot. After repeated cycles of heating hysteresis in $\rho(T)$ and $E_T(T)$ plots disappears.

If the MWNT – PTFE composite material was deformed by rolling, and this deformed material combined with starting non-deformed composite, thermocouple was formed. Its thermo-electromotive force did not exceed 1 $\mu\text{V/K}$ (Fig. 6).

Heating of samples leads to some change of E_T (Fig. 4). At that due to annealing E_T decreases by a value correlating with E_T value induced by deformation.

Specific electrical resistance of samples after cooling increases (Fig. 5). As a whole, TCR and temperature dependences of ρ and E_T are different dependent on direction, extent, and mode of preliminary deformation (compression, stretching, or rolling). So, after compression of samples to extent corresponding $\sigma \approx \sigma_{0,2}$ the first heating does not change significantly ρ , while E_T droppingly increases. After cold rolling of samples TCR for the first heating cycle have semiconductor character (Fig. 6). However, in both cases hysteresis is observed in $\rho(T)$ и $E_T(T)$ plots. Repeated heating practically does not change the character of plots.

For compressed samples with other content of MWNT the temperature dependences $\rho(T)$ и $E_T(T)$ are like to that shown in Fig. 4. Irreversible changes of ρ и E_T in this case can be explained by the structure relaxation processes and by increase of pore and microcracks concentration. As it follows from the data obtained, dependence $E_T(T)$ is insensitive to pores and microcracks, while $\rho(T)$ is sensitive to these.

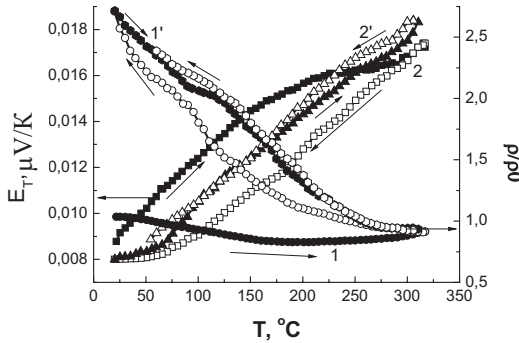


Figure 5. Heating-cooling plots of specific electrical resistance ρ (1, 1') and thermoelectromotive force E_T (2, 2') for PTFE-MWNT composite. Arrows indicate directions of temperature change.

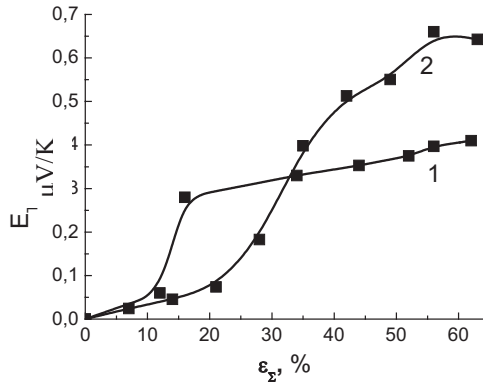


Figure 6. Dependence of thermo-electromotive force on extent of deformation for MWNT – PTFE composite materials containing 15% (curve 1) and 20% (curve 2) of MWNT.

3. Conclusions

Reinforcing of PTFE with MWNT results in considerable increase of mechanical parameters (in ~ 2 times). This proves high efficiency of MWNT as nanodimensional filler.

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MULTIFUNCTIONAL INTEGRATED FUEL CELLS ELECTRODE ON MACROPOROUS SILICON. DESIGN & TECHNOLOGY

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Abstract. The constructive and technological features of silicon electrodes of polymer electrolyte membrane fuel cell (PEMFC) are discussed. Electrodes are made with application of modern technologies of integrated circuits, and technologies of macroporous silicon. Also ways of realization of additional functionalities of electrodes to offered constructive - technological performance are considered.

Keywords: polymer electrolyte membrane fuel cell (PEMFC), porous silicon, silicon electrodes, micro fuel cells.

1. Introduction

Fuel cells (FC) on a basis of protonconducting membrane possess a number of advantages to which it is necessary to attribute high power density and relative low rate power density to weight. Distinctive feature of fuel cells in comparison with traditional batteries is division into the energy transforms device (electrodes, catalysts, a membrane and other) and the device keeping or reserving energy (as a rule, capacity with hydrogenous fuel). This circumstance allows placing FC directly on the consuming electric power device. Connection to the device of a source with hydrogen fuel allows the user to receive necessary power supplies, without what or additional procedures. Alongside with a number of other advantages PEMFC are promising, very effective power supplies for the household and mobile equipment of wide application, and also the equipment of special purpose. Nevertheless, till now the wide commercial PEMFC application is not observed. One of the reasons is the rather high cost of the PEMFC manufacturing. At that, on a share of bipolar plates, which represents plates of graphite with channels for delivery of fuel - an "anodic" electrode and removals of products of reaction - a "cathodic" electrode (Fig. 1, a position 4), is necessary up to 60 % from all cost PEMFC [1].

One of perspective ways of depreciation FC is search of new materials, and also development of new technologies for creation of highly effective electrodes. In work the constructive - technological variant of FC electrodes created on technologies of silicon integrated circuits and macroporous silicon is considered. Such approach will allow creating both super tiny power supplies, and devices with the raised level of capacity. The first is connected to opportunities modern nanotechnology, and the second with practically full exception of process of FC creation of the clamping contacts being one the main obstacles for maintenance of necessary reliability of such devices.

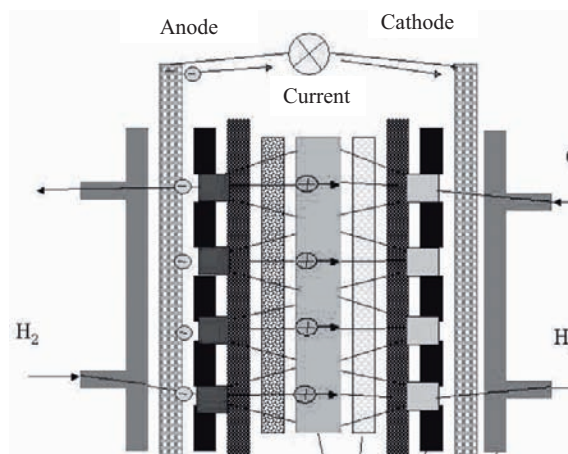


Figure 1. The traditional scheme of PEMFC.

2. Experimental

In Figure 1 the circuit of functional units traditional oxygen-hydrogen FC with «clamping contacts» is shown. Symmetrically on both sides of the polymer electrolyte membrane (PEM) (a position 1) the units included in anode and cathode electrodes are represented (positions 2-5, for simplicity units are numbered only on the one hand).

On both sides of the PEM the supports also are located (a position 6). As the catalyst for electrochemical reactions to hydrogen and oxygen electrodes platinum serves (a position 2). Good results have been received at use as the carrier of “oven soot” Vulcan XC-72, [2]. The platinum contents in platinized soot changes approximately at a level 40 %. The area of a surface on this carrier reaches up to $100 \text{ m}^2/\text{g}$ while for disperse platinum without the carrier it is usual no more than $15 \text{ m}^2/\text{g}$. Gas diffusion layer (a position 3) consist of a porous hydrophobic carbon layer and formed a catalyst active layer. Diffusion layer formed by carbon particles (soot) and polytetrafluoroethylene approximately 35wt% loaded on the carbon cloth. Porosity of diffusion layer consist approximately 60%. High porosity is especially important at use as an oxidizer of oxygen from air. Bipolar plates (a position 4) represent graphite plates with mechanically made channels for supply of fuel and oxidizer, and also removal of reaction products (water).

Volume resistance of a graphite plate is about $17 \text{ m}\Omega \text{ cm}$ [1], therefore from an underside is formed metal contact (a position 5). However the most important is minimization of electric contact of a bipolar plate with gas diffusion layer. It is achieved with the help of clamping contact, which is created, as a rule, with the help of connection by bolts. Thus contact resistance $30 \text{ m}\Omega \text{ cm}^2$ is reached at pressure of compression not less than 120 H cm^2 [1].

Offered constructively technological variant of a solid-state FC-element completely excluding clamping contacts (Fig. 2)[3]. The design of a FC-element provides presence of all functional devices represented on Fig. 1. These elements are spatially allocated in volume of silicon structure.

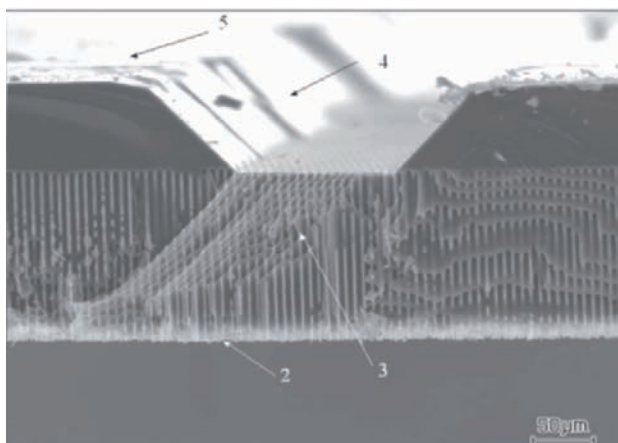


Figure 2. Cross-section view of integrated FC electrode on the basis of monocrystal macroporous silicon

The technological scheme of manufacturing of such “silicon preparation” element is shown on Fig. 3. It represents a combination of methods of modern planar technology and micro-machining methods developed with use of macroporous silicon [4]. For the experiment (100) oriented p-type silicon with 60-90 Ω cm resistivity was used. With the help of thermal oxidation and the subsequent photolithography on a surface of plates the topological structure of an arrangement of porous was formed. Using selective alkaline etching through SiO_2 mask on a surface of plates the structure of nucleating centers for the subsequent pores growth was created. After removal SiO_2 these centers represent inverse pyramids (Fig. 3a). As a result of anodic etching by a technique developed in work [5], on silicon surface the system of “ordered” pores is formed (Fig. 3b). Setting the size and pores structure, it is possible to change porosity of a layer which carries out function a “gas-diffusion layer” in structure of an integrated electrode (a position 3) in wide enough range.

For the gas-channels formation (Fig. 2 of poses 4), the plate with porous structure is exposed to repeated thermal oxidation. In result on all surfaces it is formed SiO_2 film, which on the scheme Fig. 3 by thicker line on a surface is represented. With the help of the subsequent photolithography and selective alkaline etching on a reverse side of a plate the gas-channel is formed. Thus, depth of the channel gets out such that the bottom of the channel has achieved a level of an arrangement oxidized pores (Fig. 3d). The subsequent removal SiO_2 that was a mask at alkaline etching, allows generating the gas-channel (Fig. 3e. and poses 4 on Fig. 2).

The further development is application as electrodes FC of silicon structures with gradient porosity on depth (GPSi). For the creation of GPSi dependence of pores diameter from structure of the etching solution of silicon have been used [6,7]. At the first stage etching was carried out in a mix consisting of a fluoric acid, propanole and water. Speed of etching (growth rate of pores on depth) at room

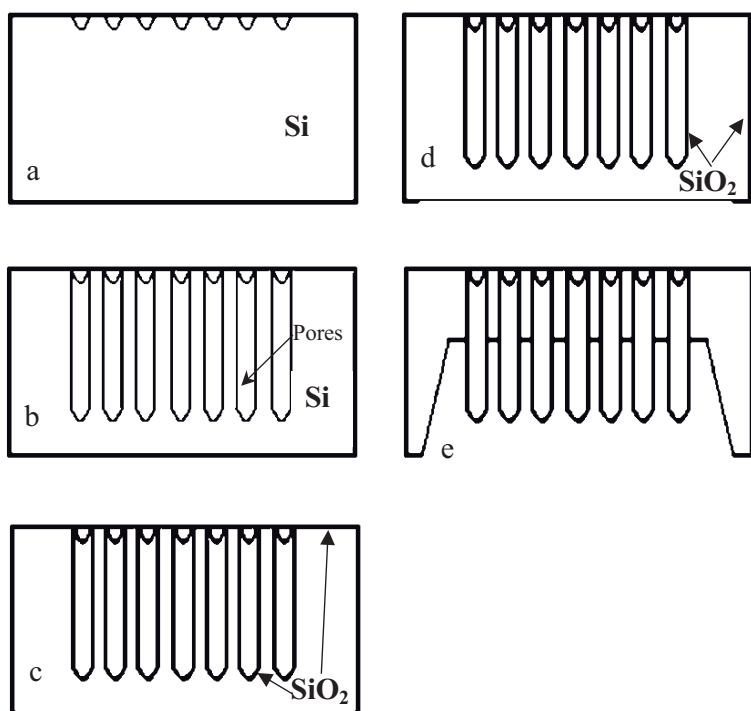


Figure 3. The technological scheme of manufacturing of multifunctional integrated FC electrode.

temperature makes 0,5-0,6 microns per minute. At the second stage replacement of a solution by a solution consisting of a mix of a fluoric acid with ethanol was carried out. Growth rate of pores in this solution makes 0,6-0,8 microns per one minute. At both stages process was carried out at the same current density and galvanostatic regime. After formation of the necessary thickness of layers the rest of a plate leaves mechanical polishing. On Fig. 4 the cross-sectional view such GPSi-structure is submitted. Two layers with various structures of pores are distinctly visible. At the first stage (the top part of structure) the uniform structure of the pores located perpendicularly to a plane of etching is formed. Average diameter of these pores is about 5 micron. At the second stage is formed time which serve as continuation of the pores generated at the first stage. However they are characterized three times by smaller diameter, except for that they are characterized by more chaotic arrangement of pores.

With the purpose of increase in a specific surface and electroconductivity of GPSi the technology of gas-phase pyrolytic sedimentation of a layer carbon fibrous nanomaterial on a surface of macropores is developed [8]. Process of sedimentation carbon fibrous nanomaterial at catalytic decomposition of the ethanol steam proceeds strictly selectively, and the received material practically does not contain some soot. The nano-fibrous layer of carbon is homogeneously enough located on all surface of macropores (Fig. 8), thickness of a layer makes about 0,1-0,4 microns and depends basically on modes of sedimentation. The layer represents a mix nano-

fibrous and nano-tubes. Thickness of fibers varied in a range 30-150 nm, external diameter of the nano-tubes makes 20-50 nm. The specific surface of carbon material, obtained in the described way exceeds $100 \text{ m}^2/\text{g}$ [7].

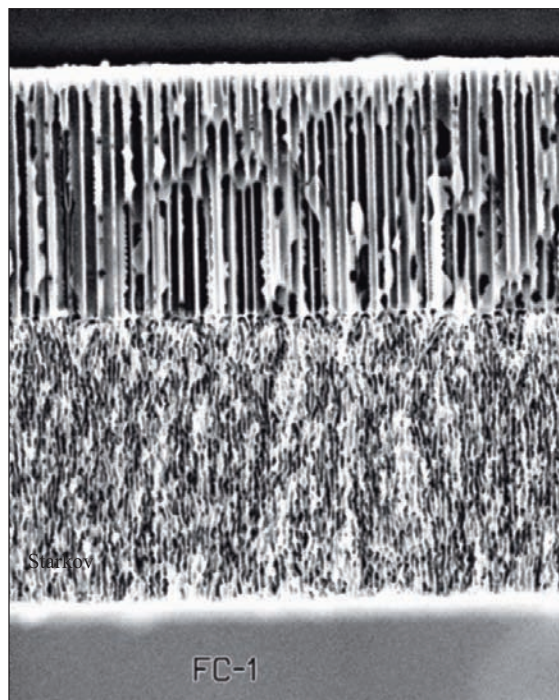


Figure 4. GPSi – structure.

Additional functionalities at electrodes appear in connection with an opportunity of formation on a surface of a bottom the gas diffusion channel a Pd-film (inset 8 on Fig. 2). Formation a Pd-film is made before removal of mask SiO_2 (a position “e”, Fig. 3). But for all that, the height of prominent hollow-pins should not exceed necessary thickness a Pd-film. Presence of this film allows applying as fuel not only pure hydrogen, but also hydrogen containing mixes.

As a base of proton conducting membrane polyvinyl alcohol (PVS) and phenolsulfonic acid (PSA) was synthesized [9]. Membrane is rendered on a surface of a catalytic layer and dries up at room temperature. As shown in [9], at ratio $\text{PVS:PSA}=4:1$ the membrane surpasses widely used in PEMFC membranes on the “Nafion” basis. Besides, experimental data testify that the solution can successfully be used as a connecting element for the anode and the cathode bonding at FC assembly.

3. Conclusions

1. Constructive-technological variant PEMFC, which completely excludes clamping contacts, is offered. A basis of suggested monolithic design PEMFC is the multifunctional silicon electrode on the basis of macroporous silicon.
2. Some technological aspects of manufacturing of such electrodes, which allow to surpass characteristics of discrete components traditional PEMFC, are considered.
3. Offered constructive-technological variant allows creating PEMFC in monolithic integrated performance.

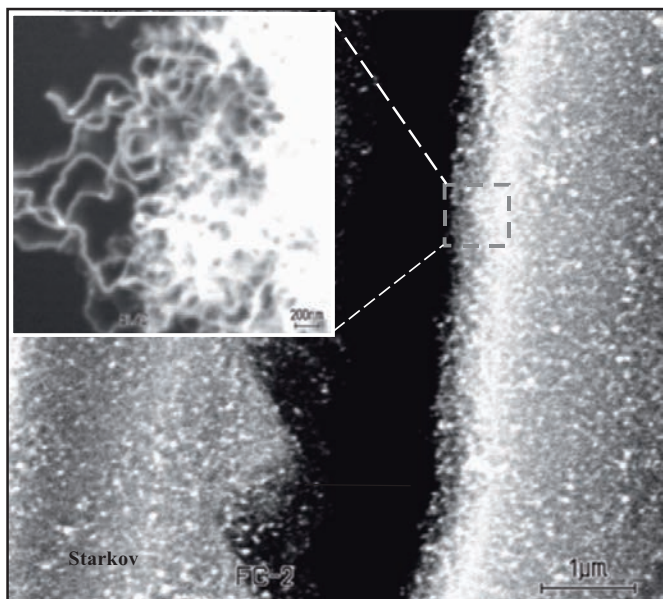


Figure 5. SEM image of carbon nanostructures on an internal surface of silicon macropores. On an insert the image received with the help of the scanning appearing through microscope

Acknowledgements

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STRUCTURAL EFFECTS IN ULTRAFINE DIAMOND UNDER THERMAL AND THERMAL-BARIC ACTIONS

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Abstract. In present work we investigate the treatment of UDD powder in a hydrogen atmosphere and during sintering of the powder both in the as-delivered condition and after annealing in hydrogen. Features of the evolution of structural reconstruction in the system of UDD particles during sintering were elucidated.

Keywords: ultrafine diamond, structural effects, treatment, hydrogen atmosphere, sintering, thermal-baric action.

1. Introduction

Today the urgency of investigations aimed at solving the problem of preparation of nanosized materials from ultradisperse diamond (UDD) powders synthesized by explosion does not raise any doubts. The complexity of the sintering process of such powders is determined to a large degree by the presence of non-diamond carbon and sorbed impurities on the surface of the initial particles [1]. The preparation of such powders to sintering usually includes pretreatments of different types that improve their process properties, including their compressibility. In the work, results of investigations of structural changes in the UDD powder during annealing in hydrogen and in vacuum and during high-pressure sintering are considered.

2. Experimental

As an initial material, UDD powders synthesized by explosion (produced by “Alite” firm, Ukraine) were used. The temperature of treatment in a hydrogen atmosphere was changed in the range 600–1000 °C. The cycle duration was 30 min. The powder both in the as-delivered condition and after annealing in hydrogen compressed under pressure 4 GPa and room temperature in the high pressure apparatus “anvil with whole” type. Then, high pressure sintering in the apparatus “toroid” type under pressure 7,5 GPa and interval of temperatures 1400–1900 °C. The state of non-diamond carbon in UDD and the evolution of the diamond phase as a result of the hydrogen thermal treatment and further temperature-force actions were studied by X-ray analysis, electron microscopy, infrared spectroscopy, X-ray spectroscopy, and adsorption-structural analysis.

3. Results and Discussion

It was established that most particles of UDD have perfect crystal faces; the main components are tetrahedrons and rectangular prisms, whose tops are often

smoothed. The range of particle size is 1-7 nm. The coarsest aggregates of particles contain microtwins along the planes (111) with a thickness of no more than 1 nm. Conglomerates of particles that have a lamellar structure contain inclusions in the form of thin plates (not larger than 500-100 nm) with a microdomain structure. In such regions, diamond is in a highly disordered state. In X-ray diffraction patterns of the powder, at $2\theta \sim 18^\circ$, a halo is observed which indicates the presence of a very disordered non-diamond form of carbon [2]. From the analysis of IR absorption spectra and x-ray $CK\alpha$ bands it follows that the interaction of surface atoms of powder particles with chemisorbed atoms and CO_2 , O_2 and other molecules took place.

It was established that the hydrogen thermal pretreatment of the UDD powder led to changes in some characteristics of diamond and non-diamond carbon. The decrease in the intensity of the reflection line (331) of diamond, the increase in the intensity of the reflection line (002) of graphite, and the weakening of the halo at $2\theta \sim 18^\circ$ indicate this. The IR spectroscopy investigations showed the influence of such treatment on the state of the functional covering on UDD particles. The determined changes in the IR-spectra can be explained by the reorientation of monomeric chains of aromatic compounds along the bond C-O-C or their packing in clusters, i.e., fragments of carbon structures of sp^2 -hybridization.

A comparison of X-ray $CK\alpha$ emission spectra of the initial UDD and hydrogen treated UDD revealed a change in the shape of $CK\alpha$ bands after the hydrogen treatment. Fig. 1a shows that peak "c" of the $CK\alpha$ -band in the powder studied is the most narrow and features "d", "d'", "f" clearly shown in the contour. Owing to the presence of two features ("d", "d'"), the spectrum of this sample is greatly differs from the those of other nanodiamonds and indicates the $CK\alpha$ splitting in this energy region. Probably, the above fact is explained by surface atoms interaction with chemisorbed atoms and molecules of CO_2 , O_2 .

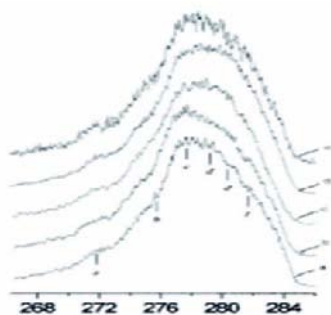


Figure 1. Average $CK\alpha$ -spectra of: a- nanodiamond Alit, b – Alit-H, c – granulated Alit, d - granulated Alit-H, e – pure diamond.

The spectral features "d", "d'" transform into broad peculiarity "d" after diamond nanopowder Alit treatment in hydrogen. As a result, after diamond nanopowder Alit treatment, its $CK\alpha$ -emission band becomes similar to reference refined diamond powder (Fig. 1e). So far as nanodiamond powders $CK\alpha$ -bands investigation was carry out at minimum anode current densities (1 mA), the unrefined diamond powder surface remained chemisorbed atoms and molecules. However, owing to electron bombardment in sample emission focus, some of chemisorbed atoms disappeared. Therefore it was important to obtain $CK\alpha$ -spectra

of synthesized unrefined diamond nanopowder at significantly greater densities of bombarded electron corresponded to anode current of 5 mA. Figure 2 presents the $CK\alpha$ -bands obtained at $I_a=1$ mA (Fig. 2a) and at $I_a=5$ mA (Fig. 2b) for the Alit diamond nanopowder. From the comparison it is obvious that, this powder $CK\alpha$ -band shape resembles that obtained from nanodiamond at anode current of 5 mA. It occurs owing to nanopowders surface refinement from chemisorbed atoms under intensive electron bombardment in consequence of chemisorbed atoms and nanodiamond surface atoms weak bonds breaking. Thus owing to nanodiamond treatment in hydrogen, it refines from chemisorbed atoms.

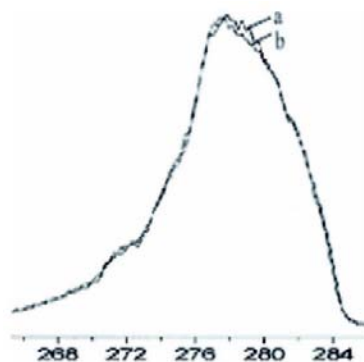


Figure 2. Coinciding of average spectra obtained: a – at $I_a=1$ mA Alit, b – the same Alit, refined by electronic beam at $I_a=5$ mA.

These results were also confirmed by the investigation of the porous structure of the diamond powders by the adsorption-structural method. It was established that the differential pore-size distribution of the initial and treated powder practically coincide, i.e., the hydrogen treatment mainly influences the state of the surface, whereas its influence on the porous structure is insignificant.

Presented in Fig. 1c the $CK\alpha$ -band of unrefined diamond powder compressed under high pressure (HP) shows that $CK\alpha$ -band peak significantly broadened at the expense of feature “f” width. It occurs owing to degenerated energy levels of non-bonding sp splitting of chemical bonds between surface atoms of neighbor nanoparticles after high pressure compression. The analogous spectra broadening were observed in some papers owing to titanium nitride and carbide consolidation at high temperatures. However, the total broadening to the width typical for natural massive diamond did not observed. At the same time, from Fig. 2d it is obvious that for the compressed diamond nanopowder refined in hydrogen the $CK\alpha$ -band almost completely resembles that of a natural diamond. The $CK\alpha$ -band peak after the HP compressed (HPC) powder broadened so that the feature “f” disappeared. In massive natural diamonds it also absent. It is the evidence of forming of the same chemical bands quantity as in the coarse powder owing to what neighbor’s nanoparticles levels splitting after granulation compensate $CK\alpha$ -band narrowing observed in nanoparticles with great quantity of broken bonds. The granules size of refined diamond powder is greater than one of unrefined. Thus, from comparative analysis of the $CK\alpha$ spectra of the two granulated (HPC) nanodiamonds it is obvious that the admixture of chemisorbed atoms prevents the chemical bonds between nanoparticles forming under HP compression. The significant portion of involving in the bond orbitals doesn’t participate in direct chemical bonds between

nanoparticles surface atoms owing the interaction of chemisorbed atoms with nearsurface atoms.

On the basis of the X-ray diffraction data it can be concluded that under the investigated conditions, in the initial and hydrogen-treated UDD powders, transformations in non-diamond carbon occur. With a rise in the temperature, in X-ray diffraction patterns of samples, the intensity of the halo at $2\theta \sim 18^\circ$ increases, whereas the level of the background decreases (Fig. 3).

The appearance of the line of graphite is accompanied by a decrease in the intensity of the halo, which shows the transformation of the disordered non-diamond form of carbon into the ordered graphite form.

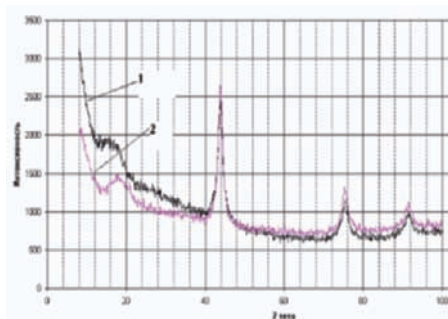


Figure 3. Typical X-ray diffraction patterns of specimens obtained on the base of the initial UDD powder under $P = 7.5$ GPa at $T = 1600$ °C (1) and 1900 °C (2).

In X-ray diffraction patterns of specimens obtained at $T \geq 1600$ °C and in SAD patterns of solid regions of specimens, the reflection lines 111 of diamond become much more narrow. This testifies to the development of reduction processes in the system of ultradisperse particles. The results of the examinations by the electron transmission electron microscopy method enable us to conclude that during sintering, in the UDD powder, transformations, that can be considered as a process of morphological relaxation of the nanodisperse powder system, occur. It is mainly realized as a result of two sequentially occurring reconstructions, namely the formation of densified aggregates of weakly interacting particles $\rightarrow$ the formation of clusters of intensively interacting particles. The last mentioned is caused by the binding of particles fact over the morphologically flat surfaces of their crystal faces with the formation of continuous surfaces of conjugation between them. In such clusters, particles are only slightly disordered. Further transformations occur both in clusters of particles and between clusters. In the first case, they are directed on “monocrystallization” of clusters, and, in the second case, on the formation of boundaries between clusters. These data evidence to the fact that under the indicated sintering conditions, only the initial stage of collective recrystallization of diamond takes place.

The differences in the structural-phase transformations during sintering under identical conditions of the UDD powder in the initial state and UDD powder after hydrogen treatment consist in the quantitative fractions of the formed graphite, dense aggregates, and clusters. As a result of the increase in the compressibility of the powder after the treatment, the fraction of dense aggregates and clusters in sintered specimens increases.

4. Conclusions

1. It was established that the treatment of the UDD powder in a hydrogen atmosphere favours the partial purification of the surface of its particles from non-diamond carbon and chemisorbed impurities.
2. Features of the evolution of structural reconstructions in the system of UDD particles and non-diamond carbon during sintering were considered.

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DEVELOPMENT OF THE APPROACH TO THE SYNTHESIS OF INDIVIDUAL ISOMERS OF BIS(ORGANO)[C₆₀]FULLERENES. BIS(AZAHOMO)FULLERENES

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Abstract. The individual regioisomers of bis(organo)-[C₆₀]fullerenes were synthesized by the reactions of fullerene C₆₀ with isocyanurato- and nitropyrimidino-substituted azides. The structures of the regioisomers were determined by ¹³C and ¹H NMR, IR and UV spectroscopy. It was shown that regioselectivity of the azides addition to fullerene framework depends on organic fragment bulk and the conjugations between organic and fullerene fragments in bis(organo)-[C₆₀]fullerene molecules.

Keywords: Fullerene; bis(organo)-[C₆₀]fullerenes, regioisomers, synthesis, structure

1. Introduction

Due to the development of fullerene chemistry it is clear that bis(organo)fullerenes as well as fullerenes and organofullerenes become the interesting area owing to unusual electronic, electrochemical, photochemical, optical and biological properties [1-3]. At first investigation stage the multiaddition to fullerenes was attractive in aesthetic standpoint – as unprecedented method for the creation of three-dimensional stereochemical definite architecture in which fullerene sphere appear as the terminal for the attaching of organic fragments on the fullerene framework. However, the following studies showed that the poly(organo)fullerenes had better filming, amphiphilic and mesomorphic properties as that of pristine fullerenes and monoorganofullerenes. Moreover, the poly(organo)fullerenes are perspective for the creation of a photovoltaic cells [4] and unusual redox systems [5]. These compounds blockade the virus [6]. However, in spite of a great attraction of the poly(organo)fullerenes the electrochemical, optical spectral and other properties of these fullerene derivatives are not properly studied. This fact mainly caused by some difficulties, appeared during the separation of individual isomers of poly(organo)fullerenes from the reaction mixture. Thus, the addition of the organic addends to the 6,6-closed mono(organo)fullerenes leads to formation of nine bis(organo)fullerenes regioisomers. The following additions theoretically result to 46 tris(organo)fullerenes regioisomers and 262 tetra(organo)fullerenes regioisomers [7]. From five to eight individual regioisomers can be separated from the bis(organo)fullerenes series [1, 8]. But the process of regioisomers separation is difficult, and these works are not numerous. It is necessary to notice that the separation of six trisadduct regioisomers of the fullerene C₆₀ and diethylbrominemalonate with 2,2'-methylenbis[(4S)-4-phenyl-2-oxazoline can be concerned to the unique investigations [9]. Two approaches are used for the regioselective addition of the various addends to fullerenes. The first approach is based on a

tendency of the organofullerenes to the retro-reactions. Due to these reactions the cyclic fragments of the fullerene sphere undergo re-form that result to the formation of more thermodynamic stable regioisomer [1]. Second approach, the so-called «tether controlled synthesis», uses the addends having definite length spacer between two functional groups [10]. On our opinion, the one more approach for the synthesis of individual bis(orgsano)fullerene regioisomers can be developed on the base of the fullerenes reactions with organic azides.

It is known [1, 11], that the addition of organic azides leads to the formation of 5,6-open monoorganofullerenes (monoazahomofullerenes). Moreover, it is shown, that in contrast to the reactions of 6,6-closed monoorganofullerenes with azides, the cycloaddition of azides to azahomofullerenes can result to the formation of one bis(organo)fullerenes isomer as the predominate product [12]. However, the question is whether regioselective cycloaddition of azide to monoazahomofullerenes depends on the structure of azide organic fragment. The present communication is devoted to the search of the answer to this question, because a little amount of isolated communications did not answer the question [13-17].

2. Experimental

Azides **1-5** were synthesized according to a previously described procedure [18-22]. ^1H NMR spectra were recorded on a Bruker AVANCE-600 spectrometer at ν_0 600.00 MHz, and ^{13}C NMR spectra – on a Bruker AVANCE-600 spectrometer at ν_0 150.864 MHz. The values δ were referred to the residual ^1H and ^{13}C signals of CDCl_3 . IR-spectra were recorded on a Bruker IFS-113V FT IR spectrometer in KBr pellets. UV spectra were recorded on a Specord UV-VIS spectrophotometer in CH_2Cl_2 and o-DCB.

Reactions of fullerene C_{60} with azides **1-5**: a mixture of 0.08 mmol of C_{60} and 0.14 mmol corresponding azides in 25 mL of anhydrous degassed o-dichlorobenzene (o-DCB) were heated for 4 h at 100°C (for azide **3**) or 180°C (for azides **1,2,4,5**). The solvent was evaporated *in vacuo*, the residue was chromatographed on a column with silica-gel to give unreacted C_{60} , corresponding mono(organo)fullerene and the fraction of bis(organo)fullerene regioisomers. The repeated chromatographing of the last fractions produced individual regioisomers of bis(organo)fullerenes.

Bisadduct 11. The column chromatography: toluene – ethyl ether (50:1) mixture as the eluent. R_f 0.21 (Sorbfil, toluene – ethyl ether (10:1)), Found (%): C, 79.84; H, 2.51; N, 9.09. $\text{C}_{82}\text{H}_{28}\text{N}_8\text{O}_6$. Calculated (%): C, 80.66; H, 2.29; N, 9.18. IR (KBr), ν/cm^{-1} : 1692 (C=O), 762 (isocyanuric ring), 527 (fullerene fragment). ^1H NMR, δ : 5.85 (ddt, 4H, 2C(8,11) H_2), 5.32 (d, 4H, 2C(9,12) H_{trans} , $^3J_{\text{H,H}} = 17.1$ Hz), 5.21 (d, 4H, 2C(9,12) H_{cis} , $^3J_{\text{H,H}} = 10.1$ Hz), 4.49 (d, 8H, 4C(7,10) H_2 , $^3J_{\text{H,H}} = 5.7$ Hz), 4.54 (m, 4H, 2C(13) H_2 , $^3J_{\text{H,H}} = 6.6$ Hz), 3.91 (m, 4H, 2C(14) H_2 , $^3J_{\text{H,H}} = 7.0$ Hz). ^{13}C NMR, δ : 148.74 (2C(4,6)); 148.46 (2C(2)); 130.82 (2C(9,12)); 119.39 (2C(8,11)); 47.74 (2C(14)); 45.12 (2C(7,10)); 41.89 (2C(13)); C_{60}N : 130.69 (2C), 132.34 (2C), 134.02 (1C) 134.66 (2C), 135.37 (2C), 136.65 (2C), 139.04 (2C), 139.20 (2C), 139.55 (2C), 139.72 (2C), 141.46 (2C), 141.65 (2C), 142.04 (2C), 142.61 (2C), 143.42 (2C), 143.58 (2C), 143.80 (2C), 143.98 (2C), 144.06 (1C), 144.14 (4C), 144.20 (4C), 144.57 (2C), 144.62 (2C), 144.82 (2C), 144.98 (2C), 145.17 (2C), 145.39 (1C), 146.85 (2C), 147.45 (2C); 160.13 (1C).

Bisadduct 12. The column chromatography: toluene – ethyl ether (50:1) mixture as the eluent. R_f 0.69 (Sorbfil, toluene – ethyl ether (5:1)), Found (%): C, 79.77; H, 2.92; N, 8.41. $C_{88}H_{40}N_8O_6$. Calculated (%): C, 80.98; H, 3.07; N, 8.59. IR (KBr), ν/cm^{-1} : 1691 (C=O), 762 (isocyanuric ring), 526 (fullerene fragment). 1H NMR, δ : 5.87 (ddt, 4H, 2C(8,11)H₂), 5.32 (d, 4H, 2C(9,12)H_{trans}, $^3J_{H,H} = 17.2$ Hz), 5.25 (d, 4H, 2C(9,12)H_{cis}, $^3J_{H,H} = 10.9$ Hz), 4.50 (d, 8H, 2C(7,10)H₂, $^3J_{H,H} = 5.8$ Hz), 4.00 (m, 4H, 2C(13)H₂, $^3J_{H,H} = 7.5$ Hz), 3.91 (m, 4H, 2C(14)H₂, $^3J_{H,H} = 7.0$ Hz), 2.06 (m, 4H, 2C(15)H₂); 1.85 (m, 4H, 2C(17)H₂); 1.71 (m, 4H, 2C(16)H₂). ^{13}C NMR, δ : 148.76 (2C(4,6)); 148.48 (2C(2)); 130.99 (2C(9,12)); 119.07 (2C(8,11)); 51.31 (2C(13)); 44.98 (2C(7,10)); 43.02 (2C(14)); 28.89 (2C(17)); 27.71 (2C(15)); 24.44 (C(16)), $C_{60}N$: 130.51 (2C), 132.26 (1C), 132.86 (2C), 134.59 (2C), 135.24 (2C), 137.10 (2C), 138.83 (2C), 139.02 (2C), 139.36 (2C), 139.58 (2C), 141.06 (2C), 141.59 (4C); 142.03 (2C), 142.68 (2C), 143.08 (1C), 143.34 (2C), 143.57 (2C), 143.73 (2C), 143.97 (2C), 144.10 (2C), 144.14 (2C), 144.19 (2C), 144.55 (2C), 144.61 (2C), 144.87 (2C), 144.96 (2C), 145.12 (2C), 145.44 (1C), 146.84 (2C), 147.61 (2C); 163.77 (1C).

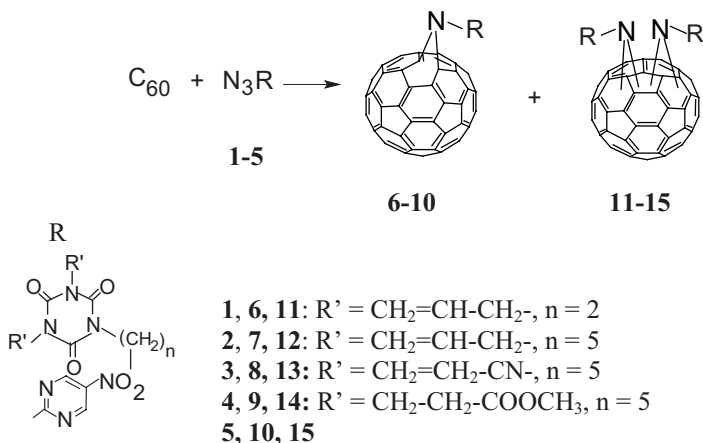
Bisadduct 13. . The column chromatography: toluene – CH₃CN (10:1) mixture as the eluent. R_f 0.32 (Sorbfil, elution toluene – CH₃CN (1:1)). Found (%): C, 76.98; H, 2.98; N, 11.60. $C_{88}H_{36}N_{12}O_6$. Calculated (%): C, 77.88; H, 2.65; N, 12.38. IR (KBr), ν/cm^{-1} : 1692 (C=O), 762 (isocyanuric ring), 527 (fullerene fragment). 1H NMR, δ : 4.25 (m, 8H, 2C(7,10)H₂, $^3J_{H,H} = 6.8$ Hz), 4.06 (m, 4H, 2C(13)H₂, $^3J_{H,H} = 7.8$ Hz), 4.03 (m, 4H, 2C(14)H₂, $^3J_{H,H} = 7.8$ Hz), 2.81 (8H, 2C(8,11)H₂, $^3J_{H,H} = 6.5$ Hz), 2.08 (m, 4H, 2C(17)H₂), 1.87 (m, 4H, 2C(15)H₂), 1.74 (m, 4H, 2C(16)H₂). ^{13}C NMR, δ : 148.24 (2C(4,6)); 148.29 (2C(2)); 116.53 (2C(9,12)); 51.29 (2C(13)); 43.41 (2C(14)); 38.37 (2C(7,10)); 28.87 (2C(17)); 27.45 (2C(15)); 24.32 (2C(16)); 16.52 (2C(8,11)); $C_{60}N$: 130.46 (2C), 132.20 (1C), 132.82 (2C), 134.57 (2C), 135.23 (2C), 137.08 (2C), 138.81 (2C), 139.00 (2C), 139.36 (2C), 139.57 (2C), 141.05 (2C), 141.54 (2C), 141.57 (2C), 142.03 (2C), 142.66 (2C), 143.35 (2C), 143.53 (2C), 143.74 (2C), 143.94 (2C), 144.03 (1C), 144.10 (2C), 144.13 (2C), 144.19 (2C), 144.55 (2C), 144.60 (2C), 144.85 (2C), 144.98 (2C), 145.12 (2C), 145.43 (1C), 146.77 (2C), 147.55 (2C); 163.60 (1C).

Bisadduct 14. The column chromatography: toluene - CHCl₃ (1:1) mixture as the eluent. R_f 0.16 (Silufol, elution with CHCl₃), Found (%): C, 73.61; H, 2.96; N, 7.63. $C_{92}H_{48}N_8O_{14}$. Calculated (%): C, 74.19; H, 3.25; N, 7.652. IR (KBr), ν/cm^{-1} : 1690 (C=O - isocyanuric ring), 1737 (C=O), 762 (isocyanuric ring), 526 (fullerene fragment). 1H NMR, δ : 4.19 (d, 8H, 2C(7,10)H₂, $^3J_{H,H} = 7.3$ Hz); 3.88 (m, 4H, 2C(13)H₂, $^3J_{H,H} = 7.3$ Hz); 3.68 (s, 12H, 2C(18,19)H₃,); 3.40 (m, 4H, 2C(14)H₂, $^3J_{H,H} = 6.7$ Hz); 2.66 (m, 8H, 2C(8,11)H₂, $^3J_{H,H} = 7.2$ Hz); 1.90 (m, 4H, 2C(17)H₂); 1.68 (m, 4H, 2C(15)H₂); 1.49 (m, 4H, 2C(16)H₂). ^{13}C NMR, δ : 170.98 (2C(9,12)); 148.54 (2C(4,6)); 148.61(2C(2)); 51.81 (2C(18,19)); 33.16 (2C(14)); 42.69 (2C(13)); 38.70 (2C(7,10)); 32.02 (2C(17)); 32.08 (2C(8,11)); 26.72 (2C(15)); 25.02 (2C(16)); $C_{60}N$: 133.67 (2C), 135.77 (2C), 136.16 (2C), 137.09 (2C), 137.28 (2C), 137.77 (1C), 137.98 (2C), 138.43 (2C), 139.14 (2C), 140.63 (2C), 141.35 (2C), 142.22 (1C), 142.58 (2C), 142.63 (2C), 142.71 (2C), 142.83 (2C), 143.03 (2C), 143.15 (1C), 143.31 (2C), 143.46 (1C), 143.57 (2C), 143.76 (2C), 144.03 (2C), 144.07 (2C), 144.20 (2C), 144.23 (2C), 144.37 (2C), 144.49 (2C), 144.64 (2C), 144.95 (2C), 146.88 (2C), 147.71 (2 C).

Bisadduct 15. The column chromatography: toluene as the eluent. R_f 0,08, (Silufol, elution with toluol, and 0.60, eluent - toluol:Et₂O, 6:1). Found (%): C, 81.22; H, 0.59; N, 10.6. C₆₈H₄N₈O₄. Calculated (%): C, 81.92; H, 0.40; N, 11.2. UV-spectrum (CH₂Cl₂), $\lambda_{\max}/\text{nm}$: 258, 325, 532. IR-spectrum (KBr), ν/cm^{-1} : 1571, 1333, 847 (NO₂), 1450 (pyrimidine cycle), 526 (fullerene fragment). ¹H NMR spectrum (CDCl₃, δ): 9.17 (s, 4H, 2C(4,6)H). ¹³C NMR spectrum: 138.50 [d, 2C(5), ² J_{CH} = 2.9 Hz], 140.00 [d, 2C(2), ³ J_{CH} = 7.2 Hz], 155.52 [d, 2C(4,6), ¹ J_{CH} = 194.7 Hz], C₆₀N: 115.44 (2C), 130.84 (2C), 135.92 (2C), 137.12 (1C), 137.92 (2C), 139.23 (2C), 139.94 (2C), 140.04 (1C), 140.94 (4C), 141.51 (2C), 141.72 (2C), 141.85 (2C), 142.42 (2C), 142.53 (2C), 143.32 (2C), 143.35 (2C), 143.46 (2C), 143.49 (2C), 143.61 (2C), 143.65 (2C), 143.75 (2C), 143.94 (2C), 144.55 (2C), 144.89 (1C), 144.95 (2C), 145.00 (2C), 145.05 (2C), 145.08 (2C), 145.99 (2C), 146.25 (1C); 146.30 (2C).

Earlier we have studied the reactions of fullerene C₆₀ with the isocyanurato-, phosphoryl-, pyrimidino-, nitropyrimidino-, quinoxalin-, benzopyrazine substituted azides [18-24]. As a result, both 6,6-, 5,6-closed and 5,6-open organofullerenes were synthesized, and the series of them were reduced electrochemically easier than the pristine fullerene C₆₀. Now the reactions of fullerene C₆₀ with isocyanurato- and nitropyrimidine substituted azides were used for the search of the answer to delivered question. For solving the problem the substituents in positions 1 and 3 of the isocyanurate ring and the number of methylene units between ring and azide group in isocyanurate containing azides were varied.

The reactions of azides **1-5** with fullerene C₆₀ were carried out in a solution of DCB using the excess of according azides. The products and the unreacted fullerene were separated by column chromatography. As a result, both individual monohomofullerenes **6-10** (5-10 % of the starting amount of fullerene) and individual regioisomers bis(organo)fullerenes **11-15** (10-15%) were isolated from each reaction mixture. Monohomofullerenes **6-10** were characterized earlier [18, 19, 22]. The structure of bis(organo)fullerenes **11-15** were determined by ¹³C and ¹H NMR, IR and UV spectroscopy. The composition of this compounds were established using data of elemental analysis. The mass-spectroscopy investigations did not allow to obtain the molecular ion peaks of bis(organo)fullerenes due to the weak volatility of these compounds.



According to the results of elemental analysis, compounds **11-15** are bisadducts, i.e., in each case, two azide molecules were added to the fullerene framework, and the reaction accompanied by the elimination of the nitrogen molecule. The IR spectra of these compounds did not contain the bands at 2100-2200 cm^{-1} corresponding to the azido group but contained band at 526-527 cm^{-1} characteristic for all types of organo[60]fullerenes (Fig. 1). Moreover, it should be noted, that the intensity of the fullerene sphere band (526 cm^{-1}) was far from being competitive with those of organic fragment and was half of the absorption band line strength in the monoadducts **6-10** spectra (Fig. 2).

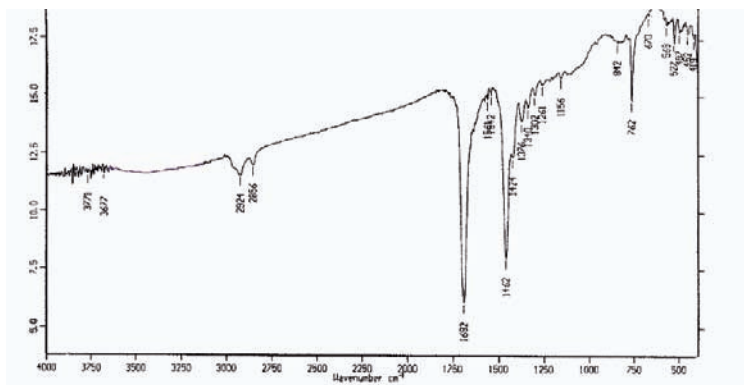


Figure 1. Bis-adduct **11** IR-spectrum (KBr).

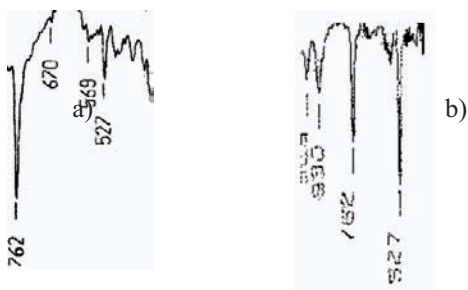


Figure 2. The fragments of bis-adduct **11** (a) and monoadduct **6** (b).

The ^1H NMR spectra of bis(organo)fullerenes **11-15** did not substantially differ from the spectra of corresponding precursory azides **1-5** and monoorganofullerenes **6-10**. At that the signals for the protons of the groups directly bonding to the N atom were slightly shifted downfield that is characteristic feature for all 5,6-open fullerene derivatives (Fig. 3).

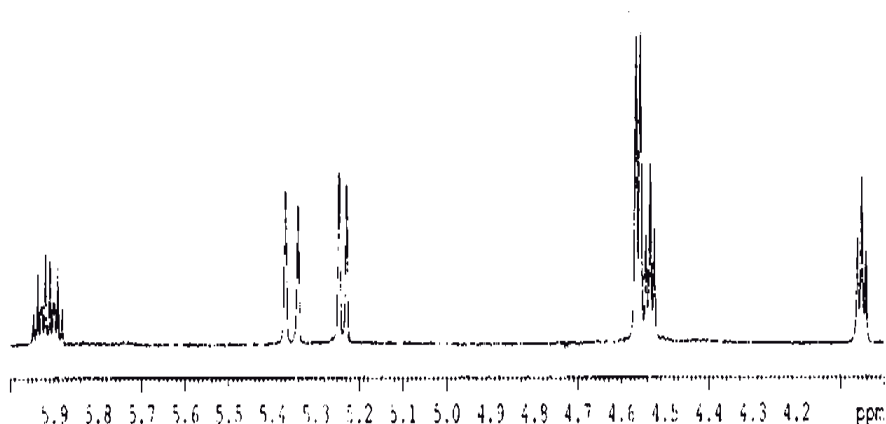


Figure 3. Bis-adduct **11** ^1H NMR spectrum (CDCl_3).

The UV spectra determination did not contain any characteristic bands at 400–800 nm. At the same time weak band at 533 nm was fixed in the UV spectrum of compound **15**, and the o-DCB and CH_2Cl_2 solutions of this compound had unusual greenish tint (Fig. 4).

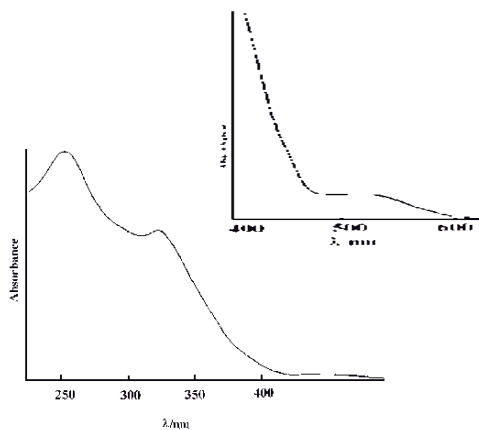


Figure 4. Bis-adduct **15** UV-spectrum (CH_2Cl_2).

Thus, the data of ^1H NMR, IR, UV spectra of the compounds **11–15** indicated to the invariability of organic fragments during the reactions of azides **1–5** with fullerene C_{60} and equivalence of two organic fragments in the bis(organo)fullerene molecules. The regioselectivity of azides addition to fullerene was determined by the data of ^{13}C NMR spectra of bis(organo)fullerenes **11–15**. The signals at δ 70–90, which were typical for sp^3 carbon atoms of the 6,6-closed fullerene derivatives,

were assented in the spectrum of these compounds. At that the ^{13}C NMR spectra exhibited signals of the sp^2 -carbon atoms of fullerene sphere, whose number and relative intensity corresponded to C_s symmetry of the bis(organo)fullerene molecules (Fig. 5). However, in spite of the same number of signals in the ^{13}C NMR spectra of bis(organo)fullerenes **11-15**, the position of some signals was unusual. Thus all signals in the ^{13}C NMR spectra of the bis(organo)fullerene **14** were fixed at δ 133-147. At the same time in addition to the signals at δ 133-147 the signals at δ 160 were observed in the spectra of allyl- and cyanoethyl substituted bis(organo)fullerenes **11-13**, and the signals at δ 115.44 and 130.84 were fixed in the spectrum of nitropyrimidine containing bis(organo)fullerene. This data show that the structures of synthesized bis(organo)fullerenes **11-15** are different.

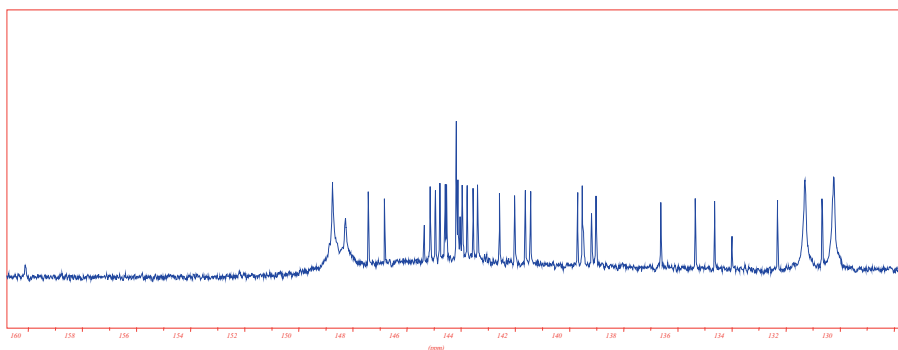


Figure 5. Bis-adduct **11** ^{13}C NMR spectrum (CDCl_3 , δ 130-165 ppm).

Four regioisomeric structures correspond to ^{13}C NMR spectra of the compound **11-15**, three of which have a 5,6-open structure **I-III**, and one regioisomer has a 6,6-open structure **IV** (Fig. 6).

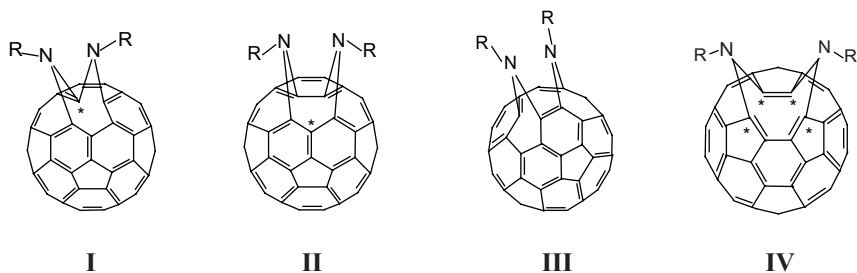
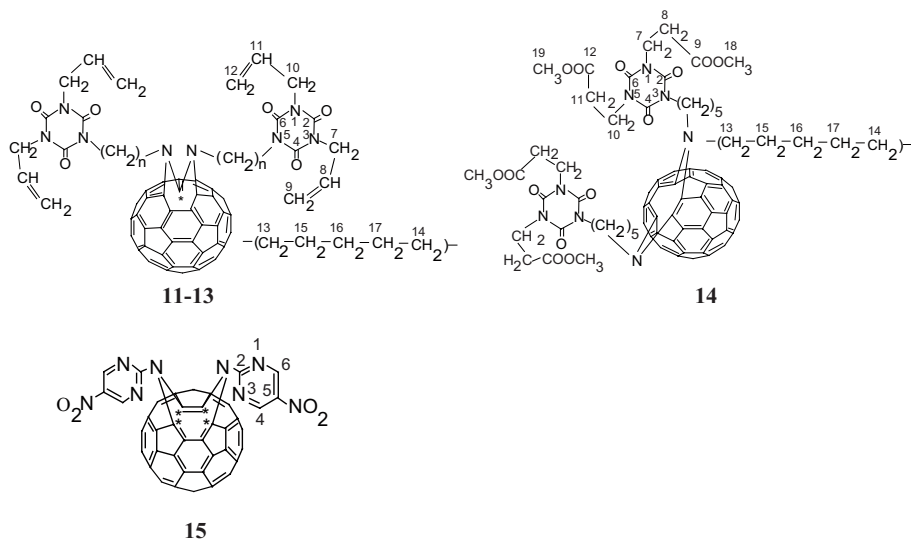


Figure 6. The possible regioisomers structure of bisadducts **11-15**.

In contrast to regioisomers **I**, **II** and **IV** the structure of regioisomer **III** does not contain the carbon atoms C^* with unusual signals in the ^{13}C NMR spectrum. The comparison of spectral data of bis(organo)fullerenes **11-15** and of known examples of the regioisomers **I-IV** [13-17] allow to assume, that the compounds

11-13 are the regioisomers **I**, the compound **14** is the regioisomer **III** and the compound **15** is the regioisomer **IV**. At that the signals at δ 160 in the ^{13}C NMR spectra of the compounds **11-13** and the signals at δ 115.44 and 130.84 in identical spectrum of the compound **15** correspond to carbon atoms C^* .



3. Conclusion

In summary, the study of the reactions of fullerene C_{60} with organic azides **1-5** showed that this type of the reactions can be considered as the approach for the synthesis of individual bis(organo)fullerene regioisomers. The structure of regioisomers depends on the structure of organic fragments in the azides molecules, the bulk of organic fragment plays the determining role in the realization of one or another regioisomer structure. However, it is necessary to point out, that the complementary conjugation of organic fragments with fullerene sphere can be determinative factors too. Most likely, that this conjugation is realized in the nitropyrimidine substituted bisadduct **15** and this fact probably determines the original structure of this regioisomer.

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BINDING OF A FLUORINE ATOM TO THE SIDEWALL OF SINGLE-WALLED CARBON NANOTUBES

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Abstract. The chemisorption problem of a single fluorine atom on the outer surface of zigzag single-walled carbon nanotubes (SWCNTs) is treated within the Anderson-Newns approach, which takes account of the intra-atomic electron interaction on the adatom. We demonstrate systematic trends in the chemisorption energy ΔE of a fluorine atom as a function of the nanotube radius for both the metallic and semiconducting SWCNTs $(p,0)$ with p ranging from 5 to 15. It is found that, in general, larger $|\Delta E|$ values are associated with the semiconducting tubes.

Keywords: Green's function methods, semi-empirical models and model calculations, chemisorption, carbon

1. Introduction

In the present paper we aim to investigate the chemisorption of a fluorine atom on the outer surface of zigzag single-walled carbon nanotubes (SWCNTs). Our treatment of this problem follows the line of the theory originally developed by Newns [1] based on a model proposed by Anderson [2] for the similar problem of a magnetic impurity in the bulk of a metal. Recently, we have employed this model to study atomic hydrogen chemisorption on the SWCNTs [3] and obtained reasonably good results for the chemisorption energy. There is also good reason to believe that the model with an appropriate set of parameters is suitable for the study of atomic chemisorption of fluorine, presented in this report.

2. Theoretical background

We adopt the same chemisorption model as in our previous work [3], which within the unrestricted Hartree-Fock approximation involves a self-consistent calculation of the electronic charge on the adatom. The basis elements needed for the calculation are the adsorbate spectral density $\rho_a^\sigma(\varepsilon)$ and the adatom Green's function $G_a^\sigma(\varepsilon)$ which are connected by the relation

$$\rho_a^\sigma(\varepsilon) = -\frac{1}{\pi} \text{Im} G_a^\sigma(\varepsilon), \quad (1)$$

where

$$G_a^\sigma(\varepsilon) = \left[\varepsilon - E_{a\sigma} - \Lambda_a^{(\nu)}(\varepsilon) + i\Delta_a^{(\nu)}(\varepsilon) \right]^{-1} \quad (2)$$

with $E_{a\sigma}$ being an effective adatom energy level and with the so-called chemisorption functions $\Delta_a^{(\nu)}(\varepsilon)$ and $\Lambda_a^{(\nu)}(\varepsilon)$ defined as

$$\Delta_a^{(\nu)}(\varepsilon) = \frac{\pi}{\sqrt{N}} V_0 \sum_{\lambda} \delta(\varepsilon - \varepsilon_{\nu\lambda}), \quad (3)$$

$$\Lambda_a^{(\nu)}(\varepsilon) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\Delta_a^{(\nu)}(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon'. \quad (4)$$

Here λ labels the electronic states of the SWCNT with the chiral index $(p, 0)$, which are described by a simple two-band $\mathbf{k} \cdot \mathbf{p}$ model based on an effective mass approximation [4], p being equal to $3M + \nu$ with integer M and $\nu = 0(\pm 1)$ for metallic (semiconducting) SWCNTs. The energy bands in Eq.(3) are given by

$$\varepsilon_{\nu\lambda}(k) = \pm \sqrt{\varepsilon_{\nu m}^2 + \gamma^2 k^2} \quad (5)$$

with

$$\varepsilon_{\nu m} = \frac{\gamma}{R} \left(m - \frac{\nu}{3} \right), \quad (6)$$

where the sign $+$ ($-$) refers to the conduction (valence) band, $m = 0, \pm 1, \pm 2, \dots \pm(p-1)$, R is the tube radius, γ is the $\mathbf{k} \cdot \mathbf{p}$ interaction parameter, k is the wave vector along the tube axis. In Eq. (3), V_0 denotes the transfer integral between the adatom orbital $|a\rangle$ and the π -orbital of the nearest-neighbouring C atom of the SWCNT, and N is equal to $4p$.

Within the Anderson-Newns model of chemisorption [1,2], the effective adatom level $E_{a\sigma}$ is shifted to

$$E_{a\sigma} = \varepsilon_a + V_{\text{im}} + (U - 2V_{\text{im}}) \langle n_{a-\sigma} \rangle, \quad (7)$$

where V_{im} is the image potential energy, U is the intra-atomic Coulomb repulsion on the adatom and $\langle n_{a-\sigma} \rangle$ is the expected occupancy of the adatom by an electron of spin $-\sigma$.

Integrating $\rho_a^{\sigma}(\varepsilon)$ with a cutoff function $g_c(\varepsilon)$ introduced by Ando et al. [5] yields

$$\langle n_{a\sigma} \rangle = \int_{-\infty}^{\mu_{\nu}} \rho_a^{\sigma}(\varepsilon) g_c(\varepsilon) d\varepsilon + \delta_{\nu, \pm 1} \langle n_{a\sigma} \rangle_{\text{loc}}, \quad (8)$$

where $\mu_{\nu} = (\gamma/3R) \delta_{\nu, \pm 1}$ and

$$\langle n_{a\sigma} \rangle_{\text{loc}} = \left[1 - \partial \Lambda_a^{(\nu=\pm 1)}(\varepsilon) / \partial \varepsilon \right]_{\varepsilon=\varepsilon_{\text{loc}}}^{-1}, \quad (9)$$

ε_{loc} being the solution of the equation

$$\varepsilon - E_{a\sigma} - \Lambda_{\sigma}^{(\nu=\pm 1)}(\varepsilon) = 0, \quad (10)$$

which determines the localized state energy in the band gap of semiconducting SWCNTs.

The $\langle n_{a\sigma} \rangle$ in Eq. (8) via $E_{a\sigma}$ is a function of $\langle n_{a-\sigma} \rangle$

$$\langle n_{a\sigma} \rangle = f(\langle n_{a-\sigma} \rangle) \quad (11)$$

and similarly the $\langle n_{a-\sigma} \rangle$ is a function of $\langle n_{a\sigma} \rangle$

$$\langle n_{a-\sigma} \rangle = f(\langle n_{a\sigma} \rangle), \quad (12)$$

so the self-consistent condition is

$$f[f(\langle n_{a\sigma} \rangle)] - \langle n_{a\sigma} \rangle = 0, \quad (13)$$

which always has a non-magnetic solution at $\langle n_{a\sigma} \rangle = \langle n_{a-\sigma} \rangle$.

Lastly, the chemisorption energy ΔE may be written as

$$\Delta E = \sum_{\sigma} \Delta E^{1\sigma} - U \langle n_{a\sigma} \rangle \langle n_{a-\sigma} \rangle - \varepsilon_a - V_{\text{im}}, \quad (14)$$

where the change in the one-electron energy produced by chemisorption is

$$\Delta E^{1\sigma} = \varepsilon_{\text{loc}}^{\sigma} + \frac{1}{\pi} \int_{-\infty}^{\mu_c} g_c(\varepsilon) \tan^{-1} \left[\frac{\Delta_a^{(\nu)}(\varepsilon)}{\varepsilon - E_{a\sigma} - \Lambda_a^{(\nu)}(\varepsilon)} \right] d\varepsilon. \quad (15)$$

3. Results and Discussion

Using the above formulas we have calculated the total chemisorption energy ΔE for a single fluorine atom adsorbed on top of a carbon atom, as well as the charge transfer from the substrate SWCNT to the adatom, which is

$$\Delta q/e = 2 \langle n_{a\sigma} \rangle - 1, \quad (16)$$

where e is the electron charge.

We have considered a number of zigzag SWCNTs ($p,0$) with p changing from 5 to 15 in order to investigate how their electronic structure, which may be either metallic or semiconducting, affects the chemisorption energy. The parameters needed for the calculation are chosen to be as follows: $U = 13.9$ eV, $V_{\text{im}} = 4$ eV and $B = 0.9$. The values of V_{im} and B are adjusted, ad hoc, so that the calculated adsorption energy ΔE for a graphene plane is equal to the experimental value (about 1.8 eV) reported in the literature. The results of our calculations are shown in Figs. 1 and 2.

As seen from Fig. 1, the charge transfer versus the radius R curves display a monotonic, almost linear, behaviour for both the semiconducting and metallic SWCNTs but with a marked difference in the slope of the corresponding curves. It is evident from Fig. 1 that there is no noticeable charge-transfer effect for the metallic SWCNTs, while for the semiconducting ones with a fairly large radius this effect is not negligible. For example, for a (14,0) nanotube with the radius 5.48 Å, about 0.1 electronic charge is transferred from the nanotube to the F adatom. This result is similar to that obtained by Jhi et al. [6] for the case of the adsorption of an oxygen molecule on a (8,0) SWCNT. Like in that case, we expect that fluorine can dope semiconducting tubes generating hole carriers. This, in turn, can significantly affect the electronic transport properties of SWCNTs that should be carefully examined. In this connection it is worthwhile to mention a recent experiment by Lee et al. [7], which showed that the resistance of a SWCNT mat prepared in the form of a pellet increases upon fluorination. Further theoretical developments are necessary to gain a proper understanding of this effect.

The curves in Fig. 2 clearly show significantly different behaviour of ΔE for metallic and semiconducting SWCNTs. For the latter $|\Delta E|$ decreases with increasing the radius (or increasing p) of the tube and eventually saturates (for large enough R) at the value corresponding to the adsorption energy of a single fluorine atom on a graphene plane. On the contrary, in the case of metallic SWCNTs $|\Delta E|$

increases with increasing R , being always smaller than $|\Delta E|$ for semiconducting nanotubes. Such contrasting behaviour is attributed to the contribution to ΔE originating from a localized state, occurring in the band gap of semiconducting SWCNTs, which leads to a remarkable decrease of ΔE and, hence, to a significant strengthening of the chemisorption bond. This finding also suggests that fluorination of semiconducting SWCNTs is energetically more effective than metallic ones, especially for the smallest (in radius) tubes.

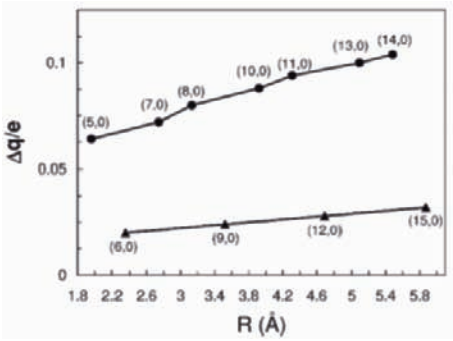


Figure 1. Charge transfer $\Delta q/e$ from the zigzag SWCNTs $(p,0)$ with $p = 5-15$ to the F atom adsorbed on their surfaces as a function of the tube radius R . The heavy dots and triangles refer to semiconducting and metallic SWCNTs, respectively. The solid lines are intended as a guide to the eye.

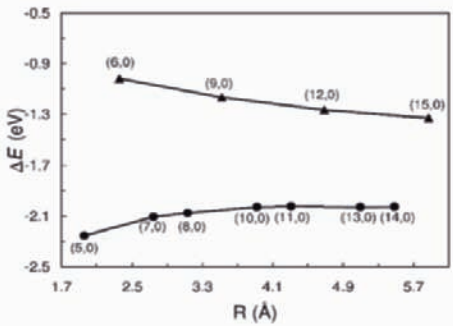


Figure 2. Chemisorption energies ΔE of a single fluorine atom adsorbed on the outer surface of the zigzag SWCNTs $(p,0)$ with $p = 5 - 15$ versus the radius R of the tubes. The solid circles and triangles refer to semiconducting and metallic tubes, respectively.

Acknowledgements

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INFLUENCE OF IMPURITIES AND DEFECTS ON ELECTRONIC STRUCTURE OF CARBON NANOTUBES

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Abstract. In frameworks of semi-empirical PM3-basis equilibrium configurations, total energy, heat of formation, energies of HOMO and LUMO orbitals, density of one-electron states (DOS) of open (12,0) carbon nanotubes with local vacancies and defects are obtained.

Keywords: carbon nanotubes, defects and vacancies, geometry and electronic structures, semi-empirical quantum calculations.

1. Introduction

The attempt of systematic theoretical investigation of the influence of defects on geometrical configuration and electronic structure of carbon zigzag and armchair nanotubes is undertaken.

The problem of classification of defects types for nanotubes is essentially more complicated than the same one for graphite monolayer. Removal of only one carbon atom can lead to appearance of two different kinds of defects, and it can be created also two different types of defects after removal of two neighboring atoms. The appearance of defects is accompanied by local and sometimes global changes of nanotubes geometry. All the computations were performed in the framework of semi-empirical PM3-method [1-2].

2. Theoretical and computational

The investigation of impurities and defects, their energetic and interactions is seemed to be very important because appearance of even one single defect can change not only value but also the type of nanotubes conductivity.

In view of wideness of information connected with the influence of impurities on geometric and physical characteristics of nanotubes [3], here are presented only results of investigations of the local defects in zigzag (12,0)-nanotubes to appear after removing one or two neighboring carbon atoms is presented. Especial attention is paid to research of vacancies as more widespread kind of breach of regularity in arrangement of atoms in nanotubes. We use for vacancies the designations which take into account the self point symmetry of defect and the way of insertion of defect into matrix. For example the designation ' $V_{a,b}D_n(\sigma)$ ' is used for vacancy 'V', which appears after removing 'a' carbon atoms and creating of 'b' chemical bonds in the defect region. The self point symmetry group of defect is dihedral group ' D_n ', and index ' σ ' is α (or β) if the angle between one of the group ' D_n ' symmetry axis and nanotube meridian direction is equal to 0° (or 60°).

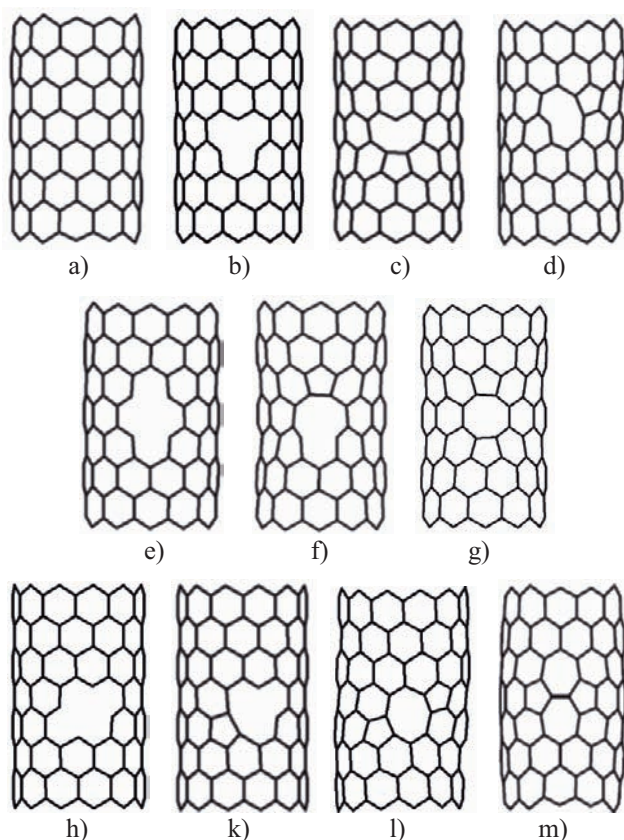


Figure 1. a) Fragment of perfect (12,0) CNT; the same fragment of (12,0) CNT with vacancies: b) $V_{1,0}D_3\alpha$; c) $V_{1,1}D_1\alpha$; d) $V_{1,1}D_1\beta$; e) $V_{2,0}D_2\alpha$; f) $V_{2,1}D_1\alpha$; g) $V_{2,2}D_2\alpha$; h) $V_{2,0}D_2\beta$; k) $V_{2,1}D_1\beta$; l) $V_{2,2}D_2\beta$ and defect m) $D_0D_2\alpha$.

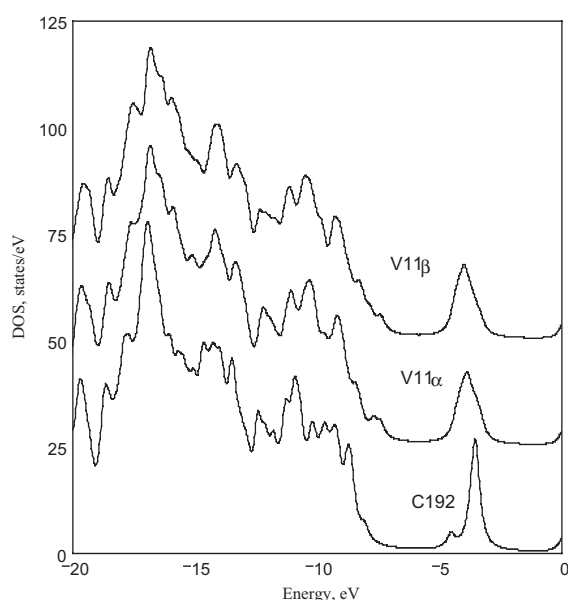
The results of calculations performed by using of empirical method MM make impression that all this configurations are really stable. But more precise PM3-computations show clearly that only configurations $V_{1,1}D_1\alpha$, $V_{1,1}D_1\beta$, $V_{2,2}D_2\alpha$ and $V_{2,2}D_2\beta$ are stable and therefore can exist.

Some the results of calculations are presented in Table 1 where the following designations are used: E – full energy; ε – mean value of full energy per one carbon atom; ΔH – heat of formation; Δh – heat of formation per one mole of carbon; E_{HOMO} , E_{LUMO} – one-electron energies of highest occupied and lowest unoccupied orbitals; $E_{gap} = E_{LUMO} - E_{HOMO}$ – the width of forbidden gap.

To make investigations more complete we consider also the same fragment of (12,0) CNT with Stone-Wales $D_0D_2\alpha$ defect [5-7].

TABLE 1. (12,0)-CNT with V_1 and V_2 vacancies

	C_{192}	C_{191} $V_{1,1}D_{1\alpha}$	C_{191} $V_{1,1}D_{1\beta}$	C_{192} $D_0D_{2\alpha}$	C_{190} $V_{2,2}D_{2\alpha}$	C_{190} $V_{2,2}D_{2\beta}$
E, eV	-22655	-22529	-22528	-22651	-22413	-22412
ϵ , eV	-118.0	-118.0	-117.9	-118.0	-118.0	-118.0
ΔH , kcal/mol	2847.3	3025.4	3047.9	2928.5	2972.6	2990.1
Δh , kcal/mol	14.8	15.8	16.0	15.3	15.6	15.7
E_{HOMO} , eV	-8.101	-7.448	-7.431	-7.976	-7.298	-7.410
E_{LUMO} , eV	-4.566	-4.357	-4.433	-4.501	-4.310	-4.376
E_{gap} , eV	3.535	3.091	2.998	3.475	2.988	3.034

Figure 2. Calculated DOS of (12,0) CNT with V_1 -vacancies.

The results of PM3-computations were used to calculate the density of one-electron states (DOS) for all considered vacancies and defect. The shapes of all calculated DOS are very similar each one to other, and small distinctions can be revealed only by the using of some kind of differential method based on comparison of the shape of given DOS with any “etalon” DOS. We can’t discuss here the results of similar analysis because the restricted volume of the paper.

As we note above the most interesting fact that occurrence of even single defect can change sometimes not only value, but type of nanotubes conductivity also [4-7].

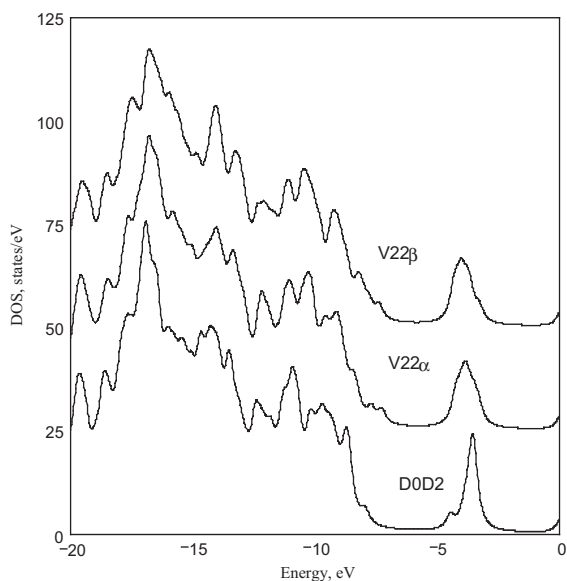


Figure 3. Calculated DOS of (12,0) CNT with V_2 -vacancies and defect D_0D_2 .

Other possible approaches to solving of the problem of description and classification of local defects in SWCNT and their junctions are in details considered in [8-11].

3. Conclusion

Done calculations point to the perspective of using nanotubes with defects for creation of nanodevices with set of various properties

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ELECTRONIC STRUCTURE OF Y-JUNCTIONS OF CARBON NANOTUBES

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Abstract. Equilibrium geometry parameters, total energies, heats of formation, energies of HOMO and LUMO orbitals, and density of one-electron states for some nanotubes Y-junctions of twig types are computed in the frames of semi-empirical quantum chemistry PM3-method.

Keywords: Y-junctions of nanotubes, defects of bonds and geometrical distortions, molecular simulation, quantum-chemical calculations.

1. Introduction

The Y-junctions of the various types are ones of the most interesting and perspective objects of modern experimental and theoretical researches because they can be used as switching elements in the future nanodevices. The paper is devoted to the theoretical studying only one of the simplest kind of Y-junctions.

2. Theoretical and computational

Quantum chemistry computations based on employing of PC Gamess version of semi-empirical PM3-method [1-2] allows to define equilibrium configuration and calculate electronic structure of some of the simplest Y-junctions of carbon nanotubes, which have slang name “twig”. On the place of nanotubes conjunction defective cycles appear. Their type, number and mutual displacement can be enough various even in comparatively simple cases. Only the part of obtained results is presented here.

The values of the following parameters are shown below in the Table 1: ε – mean value of full energy per one carbon atom; Δh – heat of formation per one mole of carbon; E_{HOMO} , E_{LUMO} – energy of highest occupied and lowest unoccupied orbitals; $E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ – the width of forbidden gap.

To get the additional possibility for comparison of the different but similar nanoconstructions we consider not only Y-junction (10,0)+(4,4) C_{396} , but T-junction (10,0)+(4,4) C_{408} also.

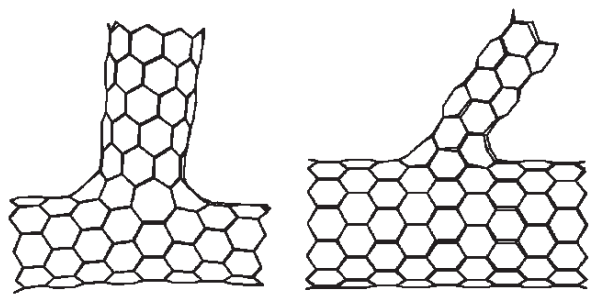


Figure 1. Equilibrium configurations of Y-junctions: a) (9,0)+(9,0) C₂₅₇; b) (12,0)+(5,0) C₂₉₁.

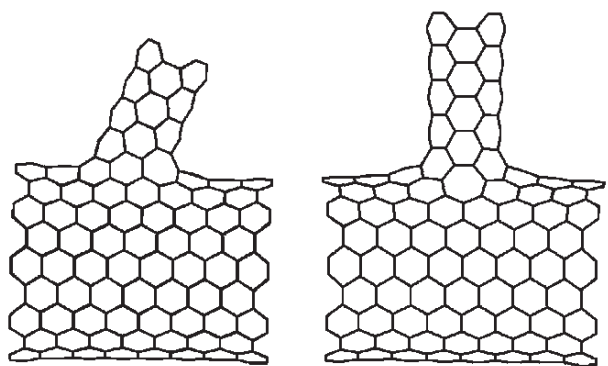


Figure 2. Equilibrium configurations of a) Y-junction (10,0)+(4,4) C₃₉₆; b) T-junction (10,0)+(4,4) C₄₀₈.

TABLE 1. Calculated characteristics of Y-junctions

	C ₂₅₇	C ₂₉₁	C ₃₉₆	C ₄₀₈
ε , eV	-117.13	-118.03	-118.14	-118.13
Δh , kkal/mol	15.77	13.90	11.98	12.35
E _{HOMO} , eV	-7.834	-7.758	-7.359	-7.126
E _{LUMO} , eV	-4.231	-4.590	-3.812	-3.932
E _{gap} , eV	3.603	3.167	3.547	3.194

The length of bonds in the region of CNTs junction, heat of formation, total energy and electronic structure essentially depends on type, number and displacement of defective cycles.

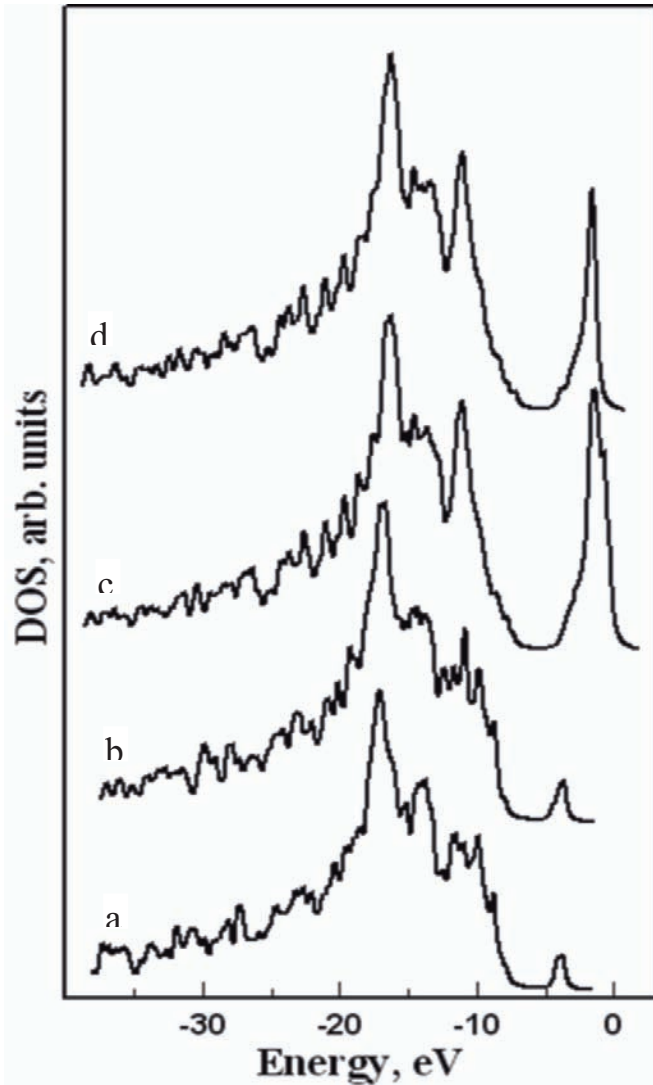


Figure 3. The shapes of calculated DOS of Y-junctions: a) C_{257} ; b) C_{291} ; c) C_{396} and d) T-junction C_{408} .

After the series of publications with the results of Papadopoulos group and other authors researches [3-7] the possibility of working out the technology of synthesis of Y-junctions of the “turnpike” type became obviously though in the near future. Measurements performed in [3-7] show clearly the perceptivities of using them as switching elements of future nanodevices.

Namely in the connection with results getting by the authors [3-7] theoretical and computational investigations of Y-junctions of any other types seems to be very actual.

3. Conclusion

Equilibrium configuration of some Y-junctions of “twig” type is defined and in the frames of semi empirical method PM3 total energy and heat of formation is calculated and their electronic structure is also defined.

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THE STRUCTURE AND PROPERTIES OF IRON ALLOYS WITH ULTRADISPERSED BY EDUCATIONS OF FREE CARBON

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Abstract. The way of reception ultradispersed of educations of free carbon in iron alloys is developed. The way is based on local melting by the concentrated sources of energy. The mechanism of formation ultradispersed of educations of free carbon is described and the influence them on properties of alloys are determined.

Keywords: carbon, pig-iron, thermocycling, melting

1. Introduction

In the first message [1] the conditions of formation ultradispersed of particles of free carbon formed in iron-carbon alloys as a result of preliminary deformation, thermocycling with phase transformations and local melting by currents of high frequency and electrical arch are considered. In cast irons, modified magnesium, the carbon particles got a spherical kind, which sizes on one - two order exceeded carbon bulbs formed at annealing diamond nanodusts [2]. From the investigated ways by most effective was melting by an electrical arch and AFC, due to which in an alloy up to 10^{11} inclusions in cm^3 , removed from each other on distance close to a diameter of inclusions were formed. The basic purposes of the present research consist in perfection of a way based on local melting, in an establishment of the mechanism of formation ultradispersed of educations of free carbon, and also in definition of properties of the received materials.

2. Experimental part

As against a technique given in job [3], in experiments widely used thermal processings on isothermal or thermocycling to a mode is accelerated cooled melting of samples. Due to this it was possible to increase up to 10^{13} cm^{-3} number of particles of free carbon, having saved thus the spherical form. Ferritic a basis, which the alloys got after short-term annealing, dispersed, that testifies to the large influence of particles of free carbon on growth ferritic of a grain. Crushing of ferrite and fine allocation of free carbon positively has had an effect on microhardness melting of sites. After annealing she corresponded to hardness ferrite-pearlite of pig-iron.

Plastic deformation of high-strength pig-iron containing 2,88%C, 2,84%Si, 0,78%Mn, 0,015%S, 0,08 %P, 0,08%Cr and 0,048%Mg, carried out hot rolling with reduction 0...75 % or forging with extract 2...9 after graphitic annealing. The

deformed and not deformed samples of pig-iron subjected to the accelerated heating by a direct electrical arch or currents of high frequency. After short-term heating in surface a thin layer the zone with the variable contents of free carbon was formed austenite-cementite-graphite. Depending on speed of cooling in surface to zone occurred crystallization on metastable or stable way. Spherical particles of free carbon being a product abnormal or normal eutectic crystallization in the latter case were formed.

3. Results and Discussion

Due to the accelerated cooling melting of high-strength pig-iron near to the rests insoluble of graphite is formed austenite-cementite eutectic, and far from them, where has taken place complete melting, are formed and dendrites superfluous austenite, between which branches is placed ledeburite and graphite (Fig. 1a). The borders melted of a zone are defined by spatial orientation of the deformed graphite. The particles extended along a contact surface, limit distribution melting. If the initial particles are placed under a corner to a contact surface, melting is distributed far deep of a sample. The large contribution brings in to complication of a structure of front melting anisotropy of graphite, heat conduction which along basic planes in some times higher, than in a cross direction [4].

The intensive education precipitates of free carbon shown in sharp increase of number of particles, promotes ferritization of a metal basis. By results of the theoretical analysis, the increase of number of particles in millions time reduces duration of disintegration cementite in hundreds time. The experiments confirm this conclusion: 10 min endurance melted of pig-iron at 850°C has appeared sufficient for end graphitization, and the cooling in air up to room temperature gives to a metal matrix ferritic a condition. Especially there are a lot of inclusions of free carbon is formed near to the rests insoluble of graphite (Fig. 1b). Decrease of the contents of carbon in connection with one more complete melting of pig-iron, and also the processes coagulation reduce number precipitates of free carbon up to 10^{10} cm^{-3} in the sites removed from deformed graphite.

At metallographic research of structure melted of sites 2 mechanisms of education of spherical particles of free carbon are revealed. In one of them, sold directly at the deformed graphite the formed particles became covered by a film austenite, that testifies to development abnormal eutectic crystallization. In other sites containing less of carbons and cooled less intensively, eutectic crystallization the education numerous dispersed dendrites austenite preceded. Crystallization of thin layers smelt, placed between branches austenite, occurred to complete division of phases, that on an example of other materials was analyzed in job [5]. Thus eutectic austenite strated on dendrites superfluous austenite, and the spherical inclusions of free carbon grew in smelt in absence austenite of an environment. Because of high-density graphite-similar precipitates in interdendritic sites the pig-iron is characterized by low mechanical properties.

On the basis of the received data the mechanism of formation ultradispersed of structures of free carbon in melted sites of the deformed high-strength pig-iron is analyzed. According to results of accounts, quantity magnesium, allocated at melting of sites with the deformed graphite, it is enough for education numerous microbubbles, on which surface at cooling an alloy the free carbon is allocated.

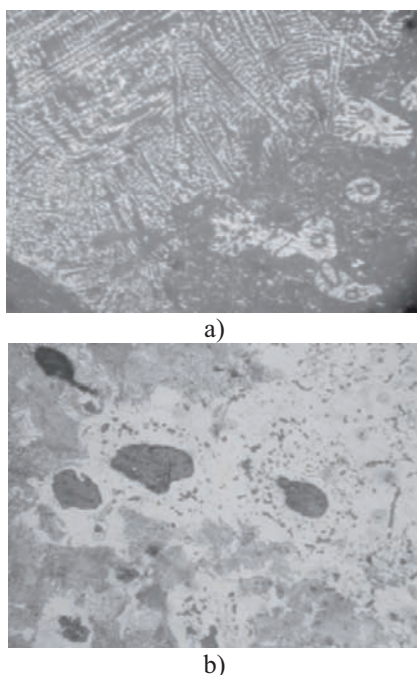


Figure 1. Microstructure preliminary deformation high-strength pig-iron after melting (a) and following annealing (b) at 850°C in during 10 min, x500.

The covering is energetically justified by a film of carbon of a surface bubble, for conducts to decrease of superficial energy of iron [6]. On formation of structure melted of pig-iron the large influence is rendered by completeness of dissolution of the deformed graphite, rate of the subsequent cooling melted of sites, branching dendrites superfluous austenite.

At hot deformation annealing of pig-iron the form ultradispersed graphitic of particles changed a little, while the large particles of graphite, present in pig-iron before heating, got a kind of thin plates. The microstructure of such sites had a lot of similar with pearlite iron-carbon of alloys, but in them the plates cementite are replaced graphitic (Fig. 2), monotonously focused in a thin pig-iron sheet. The similar structure gives to high-strength pig-iron high resistance to corrosion in water solutions of a sulfuric acid.

Meaning positive influence eutectic crystallization on structure and the properties melted of sites, are developed the following practical recommendations at the choice of technological parameters of processing of the deformed high-strength pig-iron. To the accelerated heating by the concentrated source of energy are exposed ferritic high-strength pig-irons after plastic deformation rolling or forging with reduction 30...75%. The kind of deformation defines the form formed at melting eutectic of sites. So, unilateral deposit gives to graphite a kind of plates, and reduction with turning on 90° - kind baric of particles. By the appropriate choice of a surface of heating of the deformed pig-iron focus ledeburitic or austenite-graphitic the sites arising around of deformed graphite. Choice of a surface of heating make in view of conditions of operation of products, as

resistance to corrosion, wear resistance and the cutting properties of the deformed pig-iron are anisotropy the characteristics [7].



Figure 2. Microstructure of high-strength pig-iron after hot forging.

4. Conclusion

Thermal processing with melting and subsequent annealing of the deformed high-strength pig-iron increase number of particles of free carbon up to 10^{13} cm^{-3} . The increase of number of spherical particles of free carbon is connected to education bubbles gas magnesium, transited in smelt at dissolution of the deformed graphite. The education of spherical graphite at eutectic crystallization melted of sites occurs by complete division of phases or is accompanied by formation austenite of an environment. In both cases the origin of spherical carbon particles is caused by decrease of superficial energy in connection with a covering by carbon of surface bubbles magnesium.

Acknowledgements

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EFFECT OF HYDROGEN ON DELAYED FRACTURE OF MARAGING STEELS

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Abstract. Influence of thermoplastic treatment conditions in various corrosive media on tendency of maraging steels to delayed fracture has been investigated. Parameters of the treatment that are optimal for the improvement of the structural strength of steels have been determined.

Keywords: maraging steels, hydrogen, delayed fracture

1. Introduction

Semi-finished items and products from high-strength materials may undergo fracture due to low stresses or residual stress without a noticeable macroscopic plastic pre-deformation. This type of failure which starts some time after the beginning of action of a permanent stress (lower than the yield point, but higher than a threshold value) at temperatures close to the room one is called delayed fracture (DF). DF is characterized by macro-brittle fracture. There are incubation in the DF, when crack initiation is prepared, the stage of under critical (sub-critical) growth of one or several cracks, and the stage of supercritical development of the principal crack resulting in the complete fracture of a product.

Similar to the hardened carbon steels, the maraging steels (MAS) based on Fe-Ni-, Fe-Cr-Ni- and Fe-Ni-Co- solid solution tend to DF, the sensitivity to DF being dependent on the temperature of ageing [1-3]. Brittle intergranular fracture of the steels, especially with an increased content of titanium, can be observed during the tests of low deformation rates and under a static loading. The tendency to brittle intergranular fracture abruptly increases when going from the tests in vacuum to those in air or aqueous media [3]. That's why the resistance to DF is one of the criteria to be determined to estimate the structural strength of MAS.

2. Experimental

The investigated were commercial steels of quality $\text{Fe}_{76.5}\text{Ni}_{18}\text{Mo}_4\text{Ti}_{1.5}$, $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ and $\text{Fe}_{74.7}\text{Ni}_{18}\text{Co}_3\text{Mo}_3\text{Ti}_{1.3}$. Steel $\text{Fe}_{76.5}\text{Ni}_{18}\text{Mo}_4\text{Ti}_{1.5}$ was made by double refining: the vacuum-induction melting with the electron-beam

(EB) or vacuum-arc (VA) refining; steel $\text{Fe}_{74.7}\text{Ni}_{18}\text{Co}_3\text{Mo}_3\text{Ti}_{1.3}$ - by vacuum-induction melting; steel $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ - by vacuum remelting.

Cobalt-free steels were subjected to double quenching after 30-min holding from 920 and 820°C, while the cobalt-containing steel - to simple quenching after 1 hour holding from 820°C, in water in the both cases. Samples of steel $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ were deformed under high hydrostatic pressure (HHP) by hydroextrusion method (HE) at a vertical plant mounted on a 0.98 MN hydraulic press with the reduction ration $\varepsilon \approx 0\text{-}30\%$. The pretreatment was followed by ageing in the temperature range $T_{\text{ag}} = 350\text{-}500^\circ\text{C}$ ($\tau_{\text{ag}} = 3\text{h}$). The tendency of steels to DF was estimated in air, distilled water and 3.5 % aqueous solution of sodium chloride.

The DF and impact strength tests were done by using prismatic samples, 10 mm thick, of Charpy-type with section reduced by fatigue crack. The crack was first initiated by Drozdovsky's method. The crack was controlled along its length (1.0-1.5 mm) and by the regime of motor operation. The DF tests were done by the scheme of pure bending under constant load (the Brown method [4]). Fracture ratio was estimated by time dependences of the nominal stress in sample cross-section and by values of relative drop of the strength calculated from the curves [5] and by the average velocity of crack propagation found by the procedure described in [4]. Fracture of the tested samples was studied by the method of scanning electron microscopy using the instrument of "SUPERPROBE JCXA-733" type.

Figure 1 shows the results of DF tests of the MAS for example steel $\text{Fe}_{76.5}\text{Ni}_{18}\text{Mo}_4\text{Ti}_{1.5}$ (EB) in various corrosive media after ageing at $T_{\text{ag}}=480^\circ\text{C}$.

The obtained results show that the steel shows the highest tendency to fracture during the tests in water. The calculated relative drop in strength (%) under load - $(\sigma_k - \sigma_\tau) 100\% / \sigma_k$, where σ_k - average value of short-term strength; σ_τ - average value of strength under load during time τ , for the testing duration of 500 h, makes 16, 79 and 92 % for air, sodium chloride solution and water, respectively.

Fractographic analysis of the sub-critical crack growth (SCG) during the DF in the investigated steels having the lath martensite structure has shown that under the short-and long-term tests in air the viscous dimple fracture is observed. It should be, in this case, noted that during the holding under load (i.e. under the DF), the fracture is preceded by a considerable local deformation.

On the image of ruptures of samples tested in sodium chloride solution ($\tau = 70$ h) there are regions of both viscous fracture and quasi-spalling of the size similar to that of the lath. The crystallographic analysis of fracture surface has shown that in the lath the fracture goes along the planes typical of α -martensite $\{100\}_\alpha$ and the $\{110\}_\alpha$, $\{112\}_\alpha$ and $\{123\}_\alpha$ planes. At lath boundaries, the principle direction of cracking does not change. This is because the massive martensite consists of laths of six orientations, so in the adjacent planes of the lath there are planes of low indices deviated to low angles of several degrees. As a result the propagating crack "finds" a group of such planes to cross the without a deviations. The crack noticeably changes the direction of propagating when going from one lath to another where it "finds" a new group of planes where it develops more easily. A more durable holding of the samples under load in this medium does not practically change the pattern of fracture.

During steel testing in water, a change in fracture mechanism is observed. In this case, the crack propagates mainly by boundaries of the initial austenitic grain. This phenomenon is commonly related to the “dynamic impact” during the growth of martensite crystals under the hardening against austenitic grain boundary resulting in the initiation of high local microstresses [2,3]. The latter can cause microcracks at the grain boundaries, which are, as a rule, slackened by the presence of impurity segregations. There is another viewpoint [3,5] by which the tendency to DF is due to the influence of hydrogen present in steel. Hydrogen atoms, when diffusing onto the boundaries of austenitic grains, slacken the intergranular adhesion and make the formation and development of the intercrystalline cracks easier.

Table 1 lists values of the relative drop in the strength of MAS under static load in water, past different regimes of ageing.

TABLE 1. Relative drop in strength (%) of MAS under static load in water past different ageing regimes

Steel quality	No ageing	Ageing temperature, °C				
		350	400	430	450	500
Fe _{76.5} Ni ₁₈ Mo ₄ Ti _{1.5} (VA)	53	72	78	78	73	69
Fe _{74.7} Ni ₁₈ Co ₃ Mo ₃ Ti _{1.3}	6	63	94	86	86	54

Figure 2 shows dependences of the average velocity of SCG on ageing temperature. The results show that the investigated steels tend the most to DF after ageing at $T_{ag} \approx 400-430^\circ\text{C}$.

Fractographic of ruptures patterns of the investigated steels has shown that in water the DF crack develops mainly by boundaries of the initial austenitic grains. After the short-term strength tests ($\tau = 0$) on the fracture pattern of quenched samples one can see a viscous groove-like fracture. On the patterns of samples aged at T_{ag} higher than 400°C (steel Fe_{76.5}Ni₁₈Mo₄Ti_{1.5}) and at 350°C (steel Fe_{74.7}Ni₁₈Co₃Mo₃Ti_{1.3}) and tested for short-term strength there are no grooves. This may imply that the mechanism of plastic deformation has changed.

At early stages of the SCG ($\tau > 0$), in steel Fe_{76.5}Ni₁₈Mo₄Ti_{1.5}, along the direction of crack motion, the regions of viscous groove-like fracture (similar to fracture in air under the impact viscosity and short-term strength test) are changed by regions of brittle intercrystalline fracture. With increasing the time of loading ($\tau \gg 0$) the share of viscous component, in the zone of SCG, decreases. The increase of ageing temperature acts the same as the increase in holding under load (the both factors are accompanied by the increase of the level of stresses in steel): the mixed discrete fracture is changes by the continuous brittle one. The boundary of this transition is in the range of $T_{ag} \approx 400-450^\circ\text{C}$.

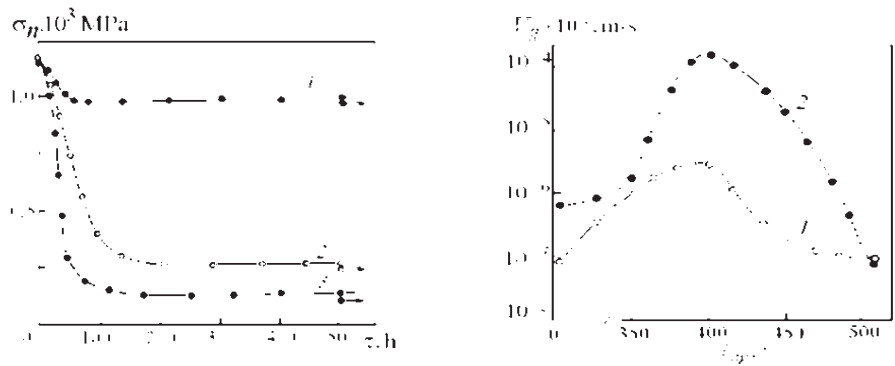


Figure 1. DF curves for steel Fe_{76.5}Ni₁₈Mo₄Ti_{1.5} after aging (T_{ag} = 480°C, τ_{ag} = 3h) in different media:

1 - air; 2 - sodium chloride solution; 3 - water; σ_n-nominal stress in cross-section of the sample.

Figure 2. Ageing temperature influence on average rate of slowing down fracture propagation in water:

1 - steel Fe_{76.5}Ni₁₈Mo₄Ti_{1.5}; 2 - steel Fe_{74.7}Ni₁₈Co₃Mo₃Ti_{1.3}.

It is a fact that in the fracture pattern of high-strength steels with SCG there are regions of microscopic viscous relief along with the intergranular fracture [6]. And the share of microscopic viscous fracture at the fracture increases with steel plasticity and values of the coefficient of stress intensity. It is believed that these regions originate from standstills and localized blunting of crack vertex due to plastic deformation of the material in the vicinity of the crack.

In steel Fe_{74.7}Ni₁₈Co₃Mo₃Ti_{1.3}, for all the investigated T_{ag} and holding under load, the SCG proceeds by the intercrystalline mechanism. Fracture of this steel is characterized by principal-crack branching taking place in samples after ageing in the temperature range 350-400°C. According to [7], the branching is typical of the cracks growing at a high velocity, and after each event of branching the propagation velocity decreases, sometimes the crack even stops. It has been noted [6,8] that crack branching favors the relaxation of stresses at crack vertex. It is seen in Fig. 2 that after the ageing at T_{ag} ≈ 400°C, for the both steels the velocity of crack propagation is the maximum, but in steel Fe_{74.7}Ni₁₈Co₃Mo₃Ti_{1.3} it is two orders of magnitude higher than in steel Fe_{76.5}Ni₁₈Mo₄Ti_{1.5}. Probably, this is the cause of stress relaxation by the way of branching in the steel with cobalt. After ageing at T_{ag} ≈ 450°C and higher no branching was observed.

The mechanical tests have shown that for MAS the character of fracture under dynamic tests – impact strength (IS) varies with the growth of T_{ag}, the same as during the short-term strength tests. This is also confirmed by the similar dependence of σ_K and IS values on ageing temperature (Fig. 3). On the σ_K (T_{ag}) and IS (T_{ag}) curves for steel Fe_{76.5}Ni₁₈Mo₄Ti_{1.5} there is a minimum corresponding to T_{ag} ≈ 430°C, while in steel Fe_{74.7}Ni₁₈Co₃Mo₃Ti_{1.3} the valley in values of the short-term strength and impact strength are wider in the temperature (practically from T_{ag}

≈ 400 to 500°C). As the results have been obtained in air and the steels maximally tend to DF in the same range of T_{ag} (see Table 1), it can be assumed that the processes responsible for the embrittlement in air also condition the fracture of steels in water.

The results of fractographic investigations show that after quenching and ageing at $T_{\text{ag}} \approx 350^\circ\text{C}$ and the short-term strength tests the steel samples have a viscous groove-like fracture. After the aging at $T_{\text{ag}} \approx 500^\circ\text{C}$ the fracture surface of as-tested samples shows fracture combined with quasi-fracture elements or a quasi-fracture implying, evidently, that there is a decrease in micro-plasticity of the matrix. In the investigated steels, the DF crack propagates inter-granularly.

Deformation under HHP by the HE method followed by ageing at $T_{\text{ag}} \approx 450^\circ\text{C}$ essentially influences the fracture of MAS in corrosive medium (water) under load. Treatment of this kind results in non-monotonous increasing of such characteristics as resistance to crack propagation under the dynamic loading of IS, resistance to macro-plastic deformation under discrete loading σ_K (IS and σ_K values were measured in air), threshold stress σ_{is} characterizing the resistance to micro-plastic deformation in corrosive medium which causes the hydrogen embrittlement of the steel (on the basis of 250-h tests), and angle between two branches of DF crack, α , depending on percent reduction ε during preliminary HE. These characteristics of the structural strength have minima near $\varepsilon \approx 5$ and $\approx 20\%$ (Fig. 4).

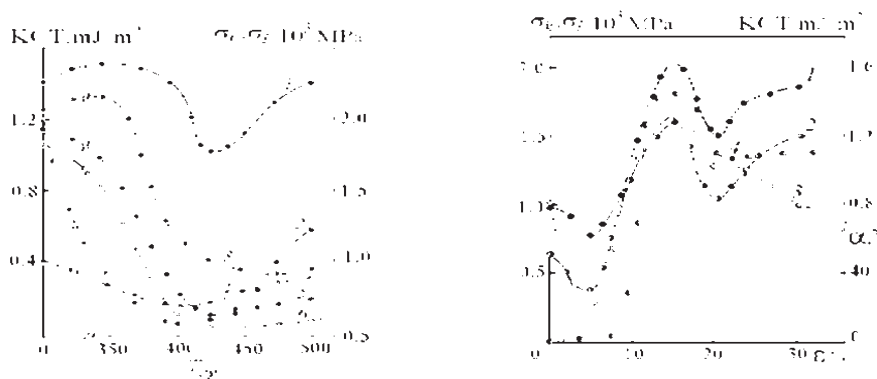


Figure 3. Ageing temperature influence on strength and viscosity of MAS: 1,2,4 - steel $\text{Fe}_{76.5}\text{Ni}_{18}\text{Mo}_4\text{Ti}_{1.5}$; 3,5,6 - steel $\text{Fe}_{74.7}\text{Ni}_{18}\text{Co}_3\text{Mo}_3\text{Ti}_{1.3}$; 1,3 - short-time strength σ_K ; 2,6 - impact strength (IS); 4,5 - threshold stress σ_{is} (on the base of 500 hours).

Figure 4. Deformation degree at hydroextrusion ε on value of IS, σ_K , σ_{is} and α of steel $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ after ageing at temperature 450°C (6 h): 1 - $\sigma_K(\varepsilon)$; 2 - $\sigma_{\text{is}}(\varepsilon)$; 3 - IS(ε); 4 - $\alpha(\varepsilon)$.

Also the character of fracture under the DF in corrosive medium is changed: samples of steel $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ after HE with $\varepsilon \leq 5$ have brittle inter-granular fracture pattern with traces of plastic deformation at some grain boundaries. The initial (undeformed) state is typical of brittle fracture (trans- and intercrystalline one) with no indication of a plastic deformation. After HE with $\varepsilon >$

5% the samples fail with quasi-fracture with a considerable share of plastic deformation during crack propagation.

The influence of chemical composition as well as causes of increased sensitivity of MAS to DF in the range of ageing temperatures were studied in articles [3,5,6]. The obtained results show that titanium influences the DF the most; the less is the influence of cobalt; molybdenum practically has no influence on DF. It is believed that in the aged MAS, the DF may result from high internal stresses originating due to the formation of intermetallic compounds of the Ni_3Ti type or from the redistribution of internal (metallurgical) hydrogen under the influence of processes of hardening-phase segregation during the ageing.

According to the results of this work and to the analyses of literary data [3,5,6], changes of medium (air by solid chloride solution and by distilled water) the same as changes of loading conditions (increase of loading duration), as well as presence of structural transformations in MAS in the low-temperature region of ageing result in the increase of the level of local internal microstresses facilitate the motion of dislocations during the origination of microcracks, which, when accumulated in the zone of preliminary fracture, results in the development of the principal crack.

It has been determined that the investigated MAS maximally tend to DF after the ageing in the temperature range $T_{\text{ag}} \approx 400\text{--}430^\circ\text{C}$, which favors essentially the increasing of the level of local internal microstresses due to the precipitation of coherent particles of the fcc $\beta\text{-Ni}_3\text{Ti}$ phase (metastable one) at early stages of ageing (it can be concluded that in the same ΔT_{ag} , there is the minimum of cracking resistance values K_{Ic}) [9]. The corrosive medium can facilitate or weaken the effect depending on the mechanism of influencing crack vertex. The highest increase of the level of internal microstresses in MAS tested in water is due to the action of hydrogen.

Abnormal sensitivity of the investigated steels to DF in different conditions of testing medium is to a considerable extent related to hydrogen embrittlement. In particular, this is indicated by a number of effects such as the grain-boundary character of fracture, jump-like growth of the crack, as well as SCG intensification under the application of cathode polarization. A lower tendency to DF during the testing in water solution of sodium chloride (as compared to water) is evidently due to partial relaxation of stresses during local anodic dissolution of the vortex of a growing crack.

The results of investigation of MAS $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ type tendency to DF in water medium have shown that the deformation of aged martensite under HHP by the HE method reduces the sensitivity to DF as a whole. The effect may be related to decreasing critical over stresses and intensified process of healing the micro- and mesoscopic defects during the deformation under pressure [10]. At the same time, it is shown that with the increase in ε during the hydrostatic extrusion, the dependence of tendency to DF varies non-monotonically for those testing conditions. Probable causes of minima occurring on the curves of corrosive-mechanical properties with ε increase are the growth of local microstresses under the deformational residual martensite $\gamma_r \rightarrow \alpha$ -transformation in the vicinity of $\varepsilon \approx 5$

% and the so-called density defect near $\varepsilon \approx 20\%$, i.e. the presence of the maximum loosening in the as-aged samples during the deformation under HHP [9].

In our model of fracture of high-strength materials [10,11], the loosening of material is due to the fact that the MAS consists of different structural elements of different scaling levels (e.g. the initial austenitic grain, lath, dislocation cell, etc.) which differently accommodate under the joint deformation. This is because the deformation mechanisms are not effective under relatively low pressures. The application of our model to investigate the HE process for high-strength materials has shown that the maximum loosening of the material, and, thus, the drop in plasticity and in viscosity characteristics are attained in some intermediate range of the critical percent reduction $\varepsilon_{cr} \approx 15 - 25\%$. In our case, the minimum of corrosive-mechanical properties of the aged MAS type $\text{Fe}_{76.1}\text{Cr}_{11}\text{Ni}_{10}\text{Mo}_2\text{Ti}_{0.9}$ is with $\varepsilon_{cr} \approx 20\%$ under the preliminary HE. Value of the critical percent reduction by HE considerably depends on the initial microporosity and on the accommodation ability of structural elements during the deformation. The observed density defect with $\varepsilon = \varepsilon_{cr}$ is because of the loosening increase with the degree of deformation ($\varepsilon < \varepsilon_{cr}$), while at higher deformations ($\varepsilon > \varepsilon_{cr}$) and, thus, higher pressures the prevailing are the processes of healing the existing defects which result in the suppression of loosening in the bulk of MAS samples.

Thus, the comparison of results of mechanical and DE tests of the investigated steels as well as the developed tendency to fracture in the quenched state afford us to assume that the important (not the only) factors responsible for the “embrittlement” of MAS are different processes taking place in the structure of steels under the high-temperature heating and deformation under HHP. The ageing facilitates the effect by increasing the level of local residual internal microscopic stresses. Effect of plastic deformation is ambiguous; it depends on testing conditions, and MAS sensitivity to DF decreases with pressure increase. If after the standard thermal treatment the investigated MAS possess relatively low tendency to DF under the static loading in air, then the corrosive medium of testing facilitates the effect depending on the mechanism of influencing the crack vertex. The appreciable loss of hardening by the investigated MAS loaded in the investigated media is connected either with the realized forced mechanism of fracture, that is as a result of decrease in the breaking stress due to the hydrogen embrittlement (water) or the deformation one at the expense of the lowering of critical deformation at crack vertex by the mechanism of local anodic dissolution (sodium chloride solution).

It should be noted that among possible reasons of the tendency of MAS to DF during the testing in air there may be “external” diffusion-active hydrogen formed during the interaction of adsorbed atmospheric moisture with chemical elements that are steel components [12]. Therefore, in this case, the DF of MAS can be treated as a particular case of corrosion cracking under the stress. The process of grain-boundary embrittlement results from both the formation of brittle titanium hydrides and at the expense of hydrogen-weakened cohesive strength of grain boundaries in the zone of tensile stresses in front of crack vertex. The formation of titanium hydrides is accompanied by a significant volume effect. The formation is three times more intensive than for the martensite transformation [12], thus

resulting in high tensile stresses in front of crack vertex that make crack development easier. Besides, the hydride precipitations favor crack development due to reduced cohesive strength of the “hydride-matrix” phase boundary resulting from differences in the elastic-plastic properties.

This is the main difference between MAS and quenched carbon steels under the DF. In the latter case, the DF is induced by the “inner” diffusion mobile hydrogen formed during the pretreatment of the steels [12]. In this respect, the embrittlement mechanisms proposed recently [2,3,5] that are based only on the principal role of internal microscopic stresses occurring at early stages of ageing and of “internal” (metallurgical) hydrogen at the DF of MAS need be defined more correctly. Nevertheless, irrespective of real mechanisms of MAS embrittlement under DF, an effective way of reducing the tendency to hydrogen embrittlement and corrosion cracking is in decreasing the size of the initial austenitic grain and, thus, the dimensions of martensite massive and laths, the optimum decrease of titanium concentration in steel, the creation of residual compressive stresses in surface layer and in the bulk of products.

3. Conclusion

Basing on the comparison of temperature and deformation dependences of the relative drop in strength, average velocity of crack propagation as well as of threshold stress values it should be noted that the steels tend to DF the most after ageing at $T \approx 400-430^\circ\text{C}$ and after the hydrostatic extrusion with the percent reduction $\varepsilon \approx 5$ and 20 %. Difference in the behavior of MAS at the SCG stage becomes apparent from the mechanism of stress relaxation at vertex of the crack in the “hydrogenised” state. Hydrogen-induced degradation of MAS structural state is a complex problem of material science, chemistry and mechanics of materials.

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RADIATIVE CONDUCTIVITY OF C₆₀ SINGLE CRYSTAL IN WEAK MAGNETIC FIELD

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Abstract. In work C₆₀ single crystals was studied. Conductivity of C₆₀ single crystal is sensitive to low dose of ionizing irradiation. It was observed that irradiation conductivity increase in magnetic field ($B < 1$ T). The models explaining given effects were suggested.

Keywords: fullerene, electrical (electronic) properties, activation energy, defects.

1. Introduction

Fullerenes find the increasing practical application (nanotechnology, spintronics and single-electronics [1]). Thus, research of electrical properties fullerenes is very interesting. One of directions in research electrical properties of fullerenes is studying influence of the radioactive irradiation on these properties. The most of papers is a devoted to studying of influence of middle and high fluencies $F > 10^{11}$ cm⁻² on C₆₀ fullerenes electrical properties [2]. Effects, coursed by low dose of the ionizing irradiation are investigated insufficiently.

The aim of the work was to reveal and study the effect of low dose ($F < 10^{10}$ cm⁻²) irradiation on the electrical conductivity of the C₆₀ single crystal.

2. Experimental

The experiments were performed with C₆₀ single crystals of high purity (99.95% C₆₀). The crystals were grown at the Institute of Solid-State Physics of RAS.

The electric current flowing through indium contacts served as a measure of conductivity. The contacts were fixed on one of the sample surface by silver paste. The voltage U applied to the contacts was equal to 50–70 V. Samples were exposed to β -irradiation with the use of a radioactive source ⁹⁰Sr + ⁹⁰Y. The mean energy of electrons $\langle E \rangle$ was equal to 0.536 MeV. All measurements were carried out at room temperature.

Figure 1a shows the current ΔI_R increase on the dose of the β -irradiation. Saturation time increased from 5 up to 20 min when the radiation intensity is increased. Relaxation time remains constant ~ 1 h in all cases. The linear increase of C₆₀ single crystal conductivity on intensity is revealed (Fig. 1b).

Beta-stimulated conductivity of C₆₀ single crystal in an interval $230 < T < 320$ K was studied. It was found that it has termoactivated character in a fcc-phase. The value obtained of activation energy $E_{fcc} = 0.17$ eV is close to an activation energy of photoconductivity $E = 0.2$ eV [3] (Fig. 1c). A decrease of an activation energy to

$E_{sc} = 0.09$ eV was observed at temperature lower than fcc-sc phase transition ($T < 260$ -255 K).

It was found that β -conductivity of C_{60} single crystal is sensitive to magnetic field (MF) $B < 1$ T. The increase in β -conductivity up to 3.5 % was observed in MF. The dependence of β -conductivity on B reached saturation at 0.2 T (Fig. 1d). The charge carriers' mobility in MF can not be the reason of MF influence on the C_{60} conductivity. Indeed, the relative change of conductivity in organic crystals caused by the change of trajectories of free charge carriers in MF $B \sim 0.1$ -1 T, is $\Delta\sigma/\sigma \sim 10^{-10}$ for typical C_{60} carriers mobility $u \sim 10^{-2}$ cm²/V·s, while the experimental values exceeded $3 \cdot 10^{-2}$. Influence of MF orientation and direction of electric field on current value was absent, that should be typical for galvanomagnetic effects.

The main effect due to interaction of fast electrons with the material is determined by the ionization of molecules and the formation of point defects. An increase in the electrical conductivity can be associated with multistage collision

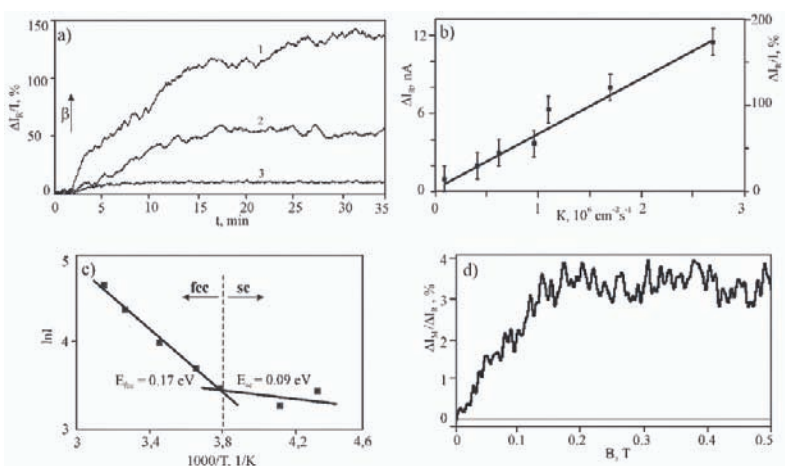


Figure 1. a) Change of an increase of C_{60} single crystal conductivity versus different electron dose rate of β irradiation K : 1 – $K_1 = 1.7 \cdot 10^6$ cm⁻²s⁻¹, 2 – $K = 0.9 \cdot 10^6$ cm⁻²s⁻¹, 3 – $K = 0.09 \cdot 10^6$ cm⁻²s⁻¹. Arrows indicate the instants of onset and termination of β irradiation; b) Change of an increase of C_{60} single crystal conductivity versus electron dose rate of β irradiation K ; c) Radiative conductivity vs $1/T$ of C_{60} single crystal in fcc and sc phases; d) Dependence of an increase of β - current $\Delta I_M/\Delta I_R$ on static magnetic field induction B .

ionization of molecules in the lattice of the C_{60} crystal by relativistic electrons. Under these conditions, the energy of a conduction electron produced in the initial ionizing event is sufficiently high for subsequent ionization of C_{60} molecules. The increment of the electric current in this case is estimated as $\Delta I = K \cdot e \cdot S \cdot \langle E \rangle / E_0 \sim 10^{-8}$ - 10^{-9} A, where $e = 1.6 \cdot 10^{-19}$ C is the elementary charge, $E_0 \sim 20$ eV is an energy exceeding the ionization energy of the fullerene molecule, $\langle E \rangle = 0.536$ MeV – average energy of electrons of irradiation, and S – sample area. It can be seen that the calculated increase of electric current is within the range of experimental values $I = 10^{-8}$ - 10^{-9} A. Suggested mechanism is confirmed by C_{60} single crystal conductivity on irradiation intensity results. However, the long times of rise and relaxation of the radiation-induced current has to doubt that the observed increase

in the electrical conductivity is caused only by multistage collision ionization of C₆₀ molecules. Proper allowance must be made both for already existing deep-level trapping centers of free charge carriers and for new defects arising under β -irradiation and also serving as traps for free charge carriers. It should be noted that at the beginning of β -irradiation the trapping centers are generated and filled simultaneously. After cease of β -irradiation the traps undergo thermal depletion takes part. The determination of deep levels and elucidation of the nature of radiation-induced defects in C₆₀ single crystal call for further investigation.

One of principal causes of increase of β -conductivity in MF can be magnetosensitive non-equilibrium processes connected with charges carriers transport or change of intensity of capture (or release) by traps of electrons and holes. High times of increase and decrease of β -conductivity confirm the given assumption, indicating the contribution of defect structure to β -conductivity of C₆₀ single crystal in MF.

Acknowledgements

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INFLUENCE OF SPIN DYNAMICS OF EXCITONIC STATES ON PHOTOCONDUCTIVITY OF FULLERITE C₆₀

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Abstract. It is shown, that the photoconductivity of C₆₀ single crystal essentially depends on a spin state of the intermediate electron-hole pairs. The distance between components of electron-hole pairs in states with uncorrelated spins and their lifetime were estimated as $R \geq 3.4$ nm and $\tau \sim 10^{-9}$ s.

Keywords: fullerene, electron paramagnetic resonance, photoconductivity

1. Introduction

Fullerenes and their chemical compounds are perspective materials for application in nanotechnology, spintronics and single-electronics [1]. Thus, the search of ways of high-speed, contactless, selective control of electron-optical properties of fullerene-based materials is actual problem. It is well known, that weak magnetic field (MF) with induction $B < 1$ T effectively influences electron-optical properties of some organic compounds (for instance, anthracene, tetracene, etc.) [2].

The aim of present work was to reveal and study the influence of static and microwave magnetic fields on photoconductivity of C₆₀ single crystal.

2. Experimental

Influence of weak MF on photoconductivity of fullerene C₆₀ single crystal was studied for main optical transitions of energy 2.64, 3.07, 3.87 eV forming photoconductivity spectrum [3]. For these transitions photocurrent dependences versus magnetic field induction B are shown in Fig. 1a. These field dependences evidence the modulation of singlet and triplet excitons concentration by weak MF [2] is reason of photocurrent sensitivity.

Magnetic resonance of the excited complexes of paramagnetic particles was studied by the ESR spectrometer RadioPan SE/X 2547 operated in the X-band and adjusted for the application of the PCDMR (photoconductivity-detected magnetic resonance). The C₆₀ single crystal sample was excited at 470 nm (2.64 eV) by the light of xenon lamp transmitted through a high-aperture monochromator. The measurements were carried out at room temperature. PCDMR spectrum of C₆₀ single crystal is shown in Fig. 1b. The spectrum consists of one positive peak at $g \sim 2$ with half-width $\Delta B = 0.007$ T. Occurrence of PCDMR signal most probably relates to $\Delta m_s = \pm 1$ spin transitions in electron-hole pairs, which are produced during the free charge carriers generation. The half-width ΔB makes it possible to estimate the lifetime of these intermediate complexes as $\tau = h/(g\mu\Delta B) \sim 10^{-9}$ s, where μ - Bohr magneton.

It was revealed, that the photocurrent increases in MF $B=0.4$ T have a maxima in external electrical fields (EF) at 4.2×10^4 , 3.1×10^4 and 2×10^4 V/m at excitation by light with photon energies 2.64, 3.07, 3.87 eV accordingly (Fig. 1c).

Influence of MF and EF on the photoconductivity of C_{60} single crystal can be presented as the following scheme. Light absorption gives rise to singlet (S) charge-transfer (CT) excitons. At the same time the more energy of quantum of excitation light, the more distance between electron and hole in the pair. Because of interaction with lattice, defects and surface the part of singlet CT-excitons are transferring to triplet state (T_0). Generally, in molecular crystals recombination from singlet state, S, occurs more effectively than from triplet, T, one. The role of MF can be reduced to increase of population of T_0 state due to intercombination transitions between S and T_0 states caused by distinction of CT-exciton's components g-factors. This results in an increase a probability of pair dissociating into free charge carriers and in decrease a probability of electron-hole recombination and, as a consequence, in an enhancement of the photoconductivity in the presence of a MF. Resonant microwave magnetic field includes $T_{\pm 1}$ Zeeman levels in spin conversion. Transitions between $T_{\pm 1}$ and T_0 deplete mixed state S- T_0 and increase the yield of triplet CT-excitons. It explains the appearance of positive ESR signal on photoconductivity of fullerene C_{60} single crystal.

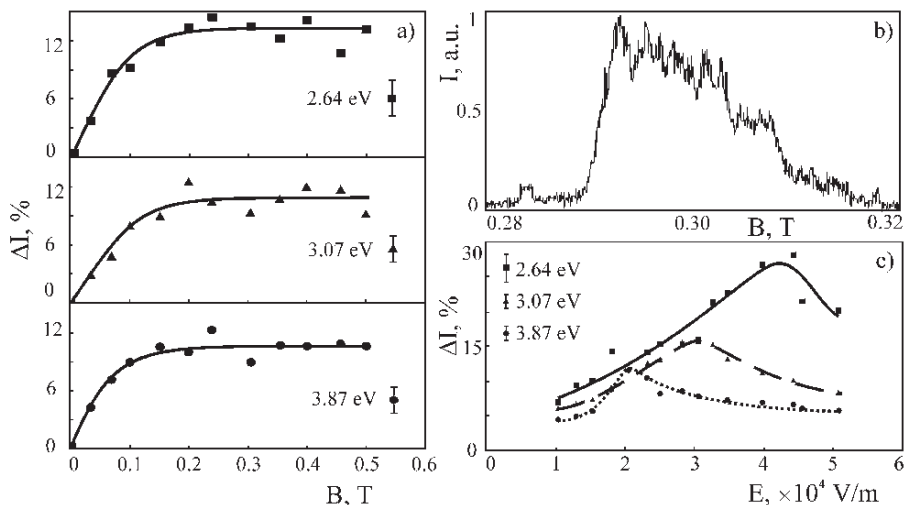


Figure 1. a) Magnetic field dependences of photocurrent for optical transitions with energies 2.64 eV, 3.07 eV and 3.87 eV; b) PCDMR spectrum of C_{60} single crystal (microwave frequency ~ 8.99 GHz); c) Electric field dependences of photocurrent for optical transitions with energies 2.64 eV, 3.07 eV and 3.87 eV.

Necessary requirement of efficient influence of MF on photoconductivity according to the mechanism is the absence of spin system's thermolysation during the time particles stay in the pair and, simultaneously, high enough rate of S – T transitions: the lifetime τ of particles' pair must be longer than time needed for mixing of the spin states τ_{ev} , but shorter than the relaxation time τ_{rel} : $\tau_{ev} < \tau < \tau_{rel}$. τ_{rel} is $10^{-6} - 10^{-8}$ s for the majority of molecular crystals. In our case, τ_{ev} for fullerene C_{60} single crystal can be estimated as 10^{-10} s.

Influence of EF on magnitude of photoconductivity of fullerene C_{60} single crystal in a weak MF can be explained in the following way. Increasing intensity of electric field causes the increase of radius of initial distance r_0 between the components of electron-hole pairs and, consequently, the decrease of probability of geminate recombination. As a result, ΔI rises at small values of EF. At higher values of EF the probability of dissociation of pairs in states with uncorrelated spins increases, that causes nonlinear behavior of electrofield dependences of photoconductivity of fullerite C_{60} in MF. The distance between components of electron-hole pairs in states with uncorrelated spins was estimated as $R \geq 3.4$ nm.

Acknowledgements

This work has been supported by Governmental Research Program: "Development of Scientific Potential of the Higher Education School" (project № 717).

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ARC DISCHARGE SYNTHESIS OF METALLOFULLERENES USING A CARBON ELECTRODE WITH CHEMICALLY MODIFIED SURFACE

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Abstract. A carbon electrode covered with lanthanum carbonate is proposed to synthesize metallofullerenes of the La@C_n row. Application of the electrode allows La@C_n production with the yield of *ca.* 0.5% of the C_{60} amount. No unfavorable changes in total yield of fullerenes, amount of cathode deposit and arc parameters are observed.

Keywords: fullerene, C_{60} , C_{70} , La@C_n , arc discharge technique

1. Introduction

Application of composite electrodes in the arc discharge process is a well-known route to metallofullerenes [1]. To prepare electrodes, a graphite rod is used to be coaxially drilled, stuffed with mixture of metal oxide, graphite powder and thermosetting resin then annealed under vacuum at *ca.* 2000°C. Such procedure seems to be laborious whereas the yield of metallofullerenes is low [2]. To increase the yield, composite electrodes structure was varied [2] and new equipment was developed [3]. This work aims at further progress in this field.

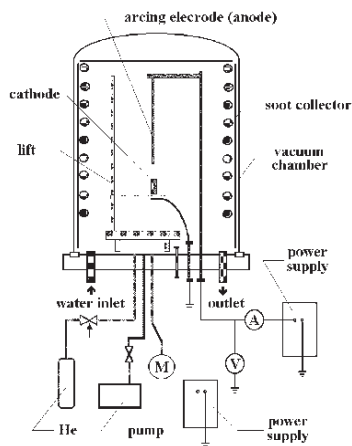


Figure. 1. Experimental set-up.

2. Experimental

The composite electrode was prepared from 100×4×6 graphite rods. Lanthanum carbonate was applied to the rod surface from aqueous suspension, dried at room temperature, mounted into a reactor (Fig. 1) and kept for 8-10 h in residual gas (10^{-2} Pa) and helium under DC of 50-70 A. To perform arc discharge process helium pressure, voltage and DC were maintained within the ranges of $2 \cdot 10^4$ - $3 \cdot 10^4$ Pa, 20-25 V and 100-150 A, respectively.

The soot obtained was collected, and carefully treated with *o*-xylene at 40°C during 24 h. Extracts were filtered, placed into analytical flasks and diluted to the constant volume of 100 ml. Concentrations of individual fullerenes in the extracts were determined by HPLC (LIQUOCHROME 2010 apparatus with a UV detector operating at 330 nm) and UV-Vis (Hitachi U2001 spectrometer) techniques.

3. Results and Discussion

UV-Vis spectra of all extracts (Fig. 2a) show a band at 1000 nm being a feature of metallofullerenes' spectra [4]. Summarizing spectral and chromatographic (Fig. 2b) data, chromatographic peaks should be referred to C_{60} (peak 2), C_{70} (peak 3) and fraction of $La@C_n$ metallofullerenes (peak 6).

The HPLC data (Fig. 3a) show that increase in lanthanum content results in increase in the C_{60} yield. Analogous trend was described in [2]. The C_{60}/C_{70} ratio (Fig. 3b) remains nearly constant in a series of experiments excepting carbonate content of 0.75 %. On the other hand, the $La@C_n/C_{60}$ ratio seems to be random (Fig. 3c) indicating, to our mind, formation of a number of different metallofullerene species with a low yield.

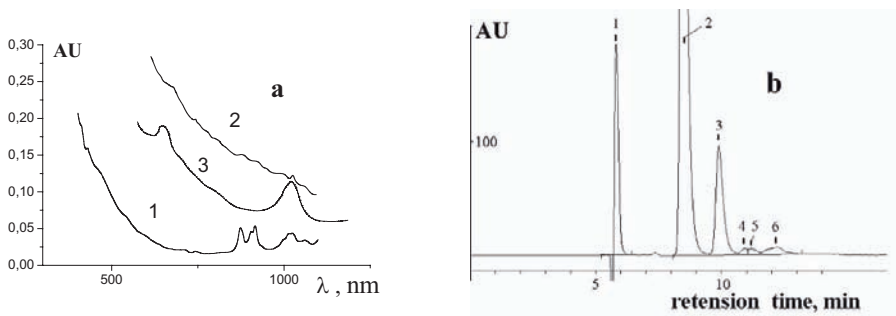


Figure 2. a - UV-Vis spectra of extracts (3 – literature), b - chromatographic data.

Experiments with lanthanum carbonate content of 0.75 and 2 % (Fig. 3) do not fit into the simple functional relationship. The phenomenon may be rationalized by the non-linear nature of the non-equilibrium systems [5, 6]. So the different stationary states in the arc and gas streams within the reactor appear. As a result, two various relationships between the C_{60} yield and lanthanum content (Fig. 3a) are found.

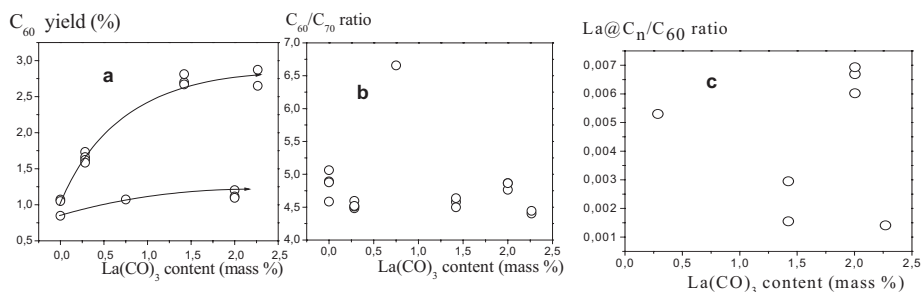


Figure 3. Efficiencies of the fullerenes synthesis.

4. Conclusion

Application of the electrode covered with lanthanum carbonate not only simplifies preparation procedure but also increases the metallofullerenes yield. Coverage of electrode surface with lanthanum carbonate does not change the C_{60}/C_{70} ratio and to some extent increase the total yield of fullerenes. Amount of cathode deposit suffers no changes also.

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ELECTROCONDUCTIVE POLYMERS AND EXFOLIATED GRAPHITE COMPOSITES AS CATALYSTS FOR OXYGEN REDUCTION

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Abstract. In present work we have investigated the reduction of oxygen at polyaniline (PANI) type electroconducting polymers (ECPs) and its composition with thermally exfoliated graphite (TEG). To explain the reasons of the catalytic activity of ECPs, a quantum-chemical modeling of ECPs and adsorption complexes of ECPs with oxygen has been performed. The calculations showed that the bond orders in chemisorbed oxygen molecules at PANI decrease by a third, and the bond length increases by more than 20% in comparison with that in a free oxygen molecule. Thus, chemisorbed oxygen molecules have fairly high degree of activation and can be readily reduced at the polymeric surface.

The above phenomena have founded a practical application for development of air-metal batteries mockups with low costs PANI/TEG composite catalysts and could find application also for some types of fuel cells.

Keywords: conducting polymers, oxygen reduction, composites, air-metal battery, fuel cells

1. Introduction

Air (oxygen) electrodes, where molecular oxygen is electrocatalytically reduced, are vital to creation of effective fuel cells and air-metal batteries. Usually noble metals such as platinum play a dominating role as electrocatalysts for the oxygen reduction in the acidic mediums. However, a serious disadvantage of Pt and other noble metals is high cost what is a main limitation for wide commercial application. That is why a search for low-cost electrocatalysts for oxygen reduction (especially from air) has been an important goal of many investigators.

Our team was the first who has founded the effect of catalytic reduction of air (oxygen) on a thin film of polyaniline (PANI) during investigation the mechanism of current- producing process at PANI [1]. The further research of this effect took possibility to clarify the electrochemical mechanism of this side reaction (two-electron reduction of O_2 to H_2O_2 and $HO_2^\cdot$) [2, 3] and to realize porous gas-diffusion electrodes with such type of catalyst and some carbon (graphite) support [4]. Our recent investigations (in press) have shown the existence of similar reaction practically at all types of conducting polymers/polypyrrole (PPy), polythiophen (PTh), poly(3-methyl)thiophen (PMeT), etc./. PANI and PTh have demonstrate the maximal catalytic activity among the other conducting polymers (CPs).

2. Experimental

The PANI was synthesized by poly-condensation of 0.4 ml aniline by 0.4 g $K_2Cr_2O_7$ in 50 ml of 1 mol·l⁻¹ HCl. The aniline concentration was not higher than 0.5M. Potassium dichromate was used as chemical oxidant. The polymer was extracted from the reaction medium by filtering the solution. The precipitate was then washed several times with distilled water. Final washing was performed in ethyl alcohol and acetone. PANI was dried at a temperature of no more than 100 °C. To build a laboratory-scale model of polymer electrode, a special paste based on polytetrafluoroethylene (PTFE) emulsion was prepared. The dry PTFE residue content was 5% of ECPs weight. The experimental ECPs electrodes were made by applying the polymer paste to a current collector of graphite with 0.5cm² area. The electrochemical measurements were made in a standard three-electrode cell using a silverchloride reference electrode and a platinum counter electrode. The measurements were performed with a PI-50-1 potentiostat, PR-8 programmer and PDA XY-recorder. All potentials in the paper are given with respect to a normal hydrogen electrode (NHE).

3. Results and Discussion

From both theoretical and practical points of view, the questions on the reasons, elementary mechanisms and practical application of this phenomenon seems to be of primary interest.

3.1. ELECTROCHEMICAL INVESTIGATIONS OF PANI FILM

The catalytic activity of the PANI for the oxygen reduction reaction was first characterized by using a film PANI electrode as the working electrode in oxygen- and argon-saturated 1 M HCl solution. Fig. 1 shows cyclic voltammograms in these two solutions.

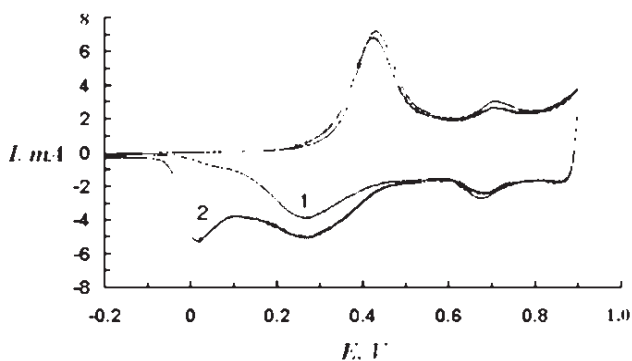


Figure 1. Cyclic voltammograms (2 mV/s) of PANI electrode in argon (1) and oxygen (2) saturated 1M HCl solution.

A reduction current is observed with two reduction peaks in the oxygen-saturated electrolyte. In the argon-saturated electrolyte, a single reduction peak at lower current density is observed. From the difference between the reduction

currents in the two solutions, the reduction current in the oxygen-saturated solution must be due to catalyzed oxygen reduction reaction.

3.2. QUANTUM-CHEMICAL MODELING

To study the possible reasons and elementary mechanisms of the catalytic activity of CPs, we have modeled the electronic structure of some molecular CPs clusters and its adsorption complexes with oxygen. A MOPAC computer complex and, in particular, the PM3 quantum-chemical program of this complex was used for calculations. The results of calculations have shown that both oxygen atoms form bonds with two more *active carbon atoms* of CP molecular cluster (so-called “bridge” model of adsorption). The total energy of system after chemical adsorption at such *active atoms* is minimal (Fig. 2).

In the CP-O_2^* complex the CP surface is an electron density donor. For example, in the case of PANI the bond orders in adsorbed O_2^* molecules decrease by about 30%, and the bond lengths L increase by about 24%. So, the adsorbed O_2^* molecules have a fairly high degree of activation and can readily interact with the protons in a solution. Further calculations show that in such case H_2O_2 compound forms even inside of adsorption complex. So, it is not necessary to spent high additional energy for formation of hydrogen peroxide.

Just H_2O_2 is a final product of electrochemical reduction of oxygen that founds a direct confirmation in the experiments.

Thus, quantum-chemical analysis confirms the mechanism of O_2 electro-reduction and gives possibility to understand the reasons of catalytic activity of such class new catalysts as PANI and some other CPs.

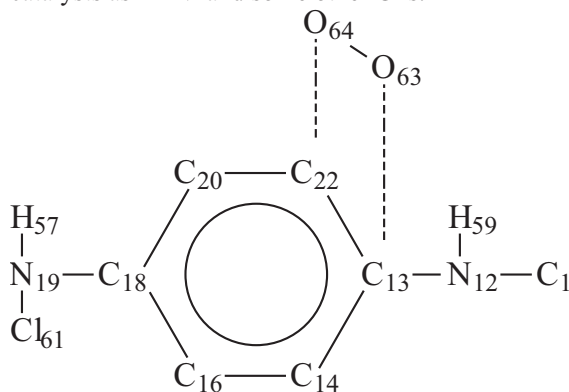


Figure 2. “Bridge model” of oxygen adsorption on the fragment of PANI structure.

3.3. DEVELOPMENT OF PANI/GRAPHITE COMPOSITES

The next important stage for the development of *PANI/graphite composites* is an investigation of influence of thickness of PANI layer (or more easy controlled parameters like PANI mass and electrochemical capacity) on the local currents of O_2 electroreduction (Table 1).

TABLE 1. The local currents of O_2 electroreduction at Graphite / PANI electrodes ($S=0.5 \text{ cm}^2$) with different mass (and electrochemical capacity) of PANI in 1M HCl solution

PANI mass, mg	PANI capacity mC	I_1 , μA	I_2 , μA	I_3 , μA
0.3	52	13	72	108
0.6	108	27	89	125
0.9	164	31	97	141
1.2	193	33	103	154
1.5	240	37	106	159
2.0	341	39	107	162

The conditions of oxygen supply to the solution: I_1 - with low O_2 content (saturated by N_2); I_2 - with middle O_2 content (saturated by O_2); I_3 - with maximal O_2 content (during O_2 bubbling on the electrode surface)

It is clear that a sharp increase of catalytic activity takes place in relatively thin layer of PANI, which corresponds to the mass of about 0.6...0.9 mg (or $Q=108...164 \text{ mC}$) per geometric surface of electrode (0.5 cm^2). Further increasing of PANI thickness (or mass) cannot increase enough the catalytic activity of porous electrode.

Our experiments, as well as analysis of the proposed theoretical model for a generalized system of porous electrode "active material – carbon additive" proved that thermally exfoliated graphite (TEG) can be one of *the most effective conductive additive and structural support* for the different new and existing active materials. The reason for such wide application of TEG is a following unique complex of TEG properties: low density, relatively high conductivity and stability to electrochemical oxidation.

4. Conclusions

The above phenomena of catalytic activity of CPs toward air (oxygen) reduction have founded a practical application for development of air-metal batteries mockups with low costs PANI/TEG composite catalysts [4]. Specific energy to be attained as primary battery is of about 150 W·h/kg for Air/PANI-Zn and 250 W·h/kg for Air/PANI-Mg batteries. The discharge curves of such batteries is practically horizontal since there are determined by the oxygen reduction potential.

We believe that new type of CPs/TEG composites will find in perspective a practical application also for some types of fuel cells.

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SOME QUESTIONS HYDRIDE REACTORS DESIGN

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Abstract. Some ideas put into designing of the basic MHHP device - a hydride reactor-sorber - are traversed in the report. Features of hydride beds are considered from the point of view of hydrogen filtration and heat exchange improvement. Designs of two sorbers - modular and monoblock are described and their effective thermal conductivity and heat transfer are evaluated. Results of experimental determination of effective thermal conductivity of hydride bed with the heat-conducting corrugated insertion are given. Parameters of installations tested with developed sorbers are briefly presented. Approaches and some results of mathematical modelling MHHP processes are presented. Achieved experimental characteristics are compared for different sorbers. It is shown that a modular sorber takes precedence over monoblock one because of essentially greater heat exchange surface.

Nomenclature

$a = \lambda_{\text{ef}}[C_p \rho]$	Thermal diffusivity of a hydride bed, ($\text{m}^2 \text{s}^{-1}$)
C_p	Heat capacity of a sorber ($\text{J kg}^{-1} \text{K}^{-1}$)
C	Hydrogen concentration, [g-atom H_2 (mole of an alloy) $^{-1}$]
d	Diameter, m
G	Coolant charge, (kg s^{-1})
K_k	Construction factor (ratio device and hydride weights)
K_{ht}	Heat conductance, ($\text{W m}^{-2} \text{K}^{-1}$)
P	Pressure, Pa
Q, P	Power, W
T, t	Temperature, ($^{\circ}\text{C}$, K)
Fo	Fourier number
Bi	Biot number
HTH, LTH	High- and Low-Temperature Hydrides
HHP	Hydride Heat Pump

Greek symbols

α	Heat transfer coefficient, ($\text{W m}^{-2} \text{s}^{-1}$)
δ	Thickness of hydride bed, wall, m
ε	Porosity
λ_{ef}	Effective heat-conductivity coefficient of a hydride bed, ($\text{W m}^{-1} \text{K}^{-1}$)
ρ	Density, (kg m^{-3})
τ	Time, s

Indexes

r	radial direction
a	axial direction
h	hydride
m	material of a skeleton of heat-conducting insertion
char	characteristic
ef	effective

Keywords: hydride, hydrogen, hydride bed, heat pump, modeling, experiment.

1. Introduction

Metal hydrides are utilized in heat engines to transform low potential (below 200°C) thermal energy into potential energy of hydrogen pressure, creation of safe hydrogen accumulators, thermochemical (thermal sorption) compressors and non-polluting heat devices (refrigerators, heat pumps, heat transformers). Designs of heat engines based on hydrides (so-called Metal Hydride Heat Pumps (MHHP)) have an obligatory component - hydride beds or more common - element with metal hydride. To provide metal hydride elements effective operation it is necessary to determine correctly their parameters.

Metal hydride element is a complex physical item, which can be described by the continuum theory equations. There are three basic processes: i) process of hydrogen filtration through a porous hydride matrix and heat-conducting inserting, ii) processes of heat application and heat abstraction from a space of hydrogenation and iii) chemical processes accompanying hydrogen sorption - desorption.

The heat-and-mass transfer mathematical model in hydride elements can be based on the laws of preservation of mass, energy conservation and the equation of hydrogenation reaction kinetics. The model, under some assumptions, will include the following equations: 1) the continuity equation (for balance of free hydrogen amount) with capacity of hydrogen source depending on sorption - desorption reaction; 2) the equation of energy, as balance of heat in microvolume (heat transfer by thermal conductivity, heat release due to reaction and convective exchange during hydrogen filtration); 3) the kinetic equation of reaction.

Solution of full model equations in general is a difficult problem. Therefore, it is important to find simplifying assumptions.

For many hydrides, the kinetics of chemical reactions at rather high temperature (above 260 K) is not a limiting stage, and it is possible to assume equilibrium in each point between free and bound hydrogen. In addition, it means that it is possible to use equilibrium P - C - T relationship for hydride. The contribution of heat transfer during filtration of hydrogen is evaluated as 5% of total transfer; therefore, it is supposed that convective transfer of heat is small in comparison with heat transfer by thermal conductivity.

Thus, processes of thermal conductivity and processes of hydrogen filtration determine processes of transfer in MHHP. Therefore, MHHP designing requires the greatest attention to these processes.

2. Features of hydride sorbers

Technical application of metal hydrides (storage, transportation, distribution and use of hydrogen in vehicles, thermosorption compressors, heat engines, etc.) requires reactors (sorbers), where chemical reactions of hydrogen sorption and desorption for heat or cold generation takes place. Mandatory elements of sorbers are body, hydride bed, elements for hydrogen flow, filtering and heat exchange, shut-off and control valves.

Basic element of a sorber is metal hydride. Beside physicochemical characteristics, it has technical characteristics (fine or coarse powder, compound or composite). Freely filled powder has the certain bulk density and is characterized by porosity in the limits of ε - 0.259 - 0.476 [1].

The alloy is failed during some cycles of hydrogen sorption - desorption and turns into powder with particles 3-4 microns. The specific surface of such powder can be estimated with assumption of their spherical shape a_0 (1.5-2.0 microns) with equivalent diameter of a particle $d_{eq} = 4\varepsilon/[a_0(1-\varepsilon)] = 1.3$ -1.6 microns. These values can be used in calculations of gas dynamics of hydrogen flow and heat exchange in a layer.

Besides, it is necessary to take into account that the initial volume of metal hydride layer can increase after hydrogen absorption for 20-30% causing "swelling" of the container, its damage and depressurization. This circumstance should be kept in mind during filling of a sorber by preferably hydrided powder.

To increase thermal conductivity of powder layer metal powders of copper, aluminium are added. Composites are compacted in pellets, which can be sintered in addition. Their main characteristics are coefficient of effective thermal conductivity and coefficient of gas-permeability. The weight fraction of powder in such compacts serves as the controlled parameter, and it has the optimum, when gas-permeability does not worsen sharply at acceptable thermal conductivity. Encapsulation of hydride powder by material with high thermal conductivity followed by compaction of pellets and their sintering is also used.

Other important element of a design is the hydrogen manifold. From the equation of a filtration it becomes clear that it is necessary to reduce hydrogen pressure gradient, i.e. to reduce length of hydrogen filtration. It was found experimentally that sorber productivity with a longitudinal manifold for hydrogen gathering and distribution in comparison with hydrogen filtration from only a sorber end face is by one and a half order of magnitude greater. Joint use of a heat-conducting insert and hydrogen manifold raises processes rate to ~2500 times. Increase of the central manifold diameter from 2-4 mm to 8-10 mm accelerates processes in hydrides approximately twice [2].

The problem of hydrogen filtration through bed is solved simultaneously with manifold mounting. Pore size in filtering bed should not exceed 1-3 microns, i.e. their size should be less than size of particles of hydride powder. The filter should have two layers - the first layer serves as a membrane with pores size 1-2 microns, and the second layer with pores size by one and a half order of magnitude greater is a bearing course of a manifold.

The important element of a hydride bed is the heat-conducting insert or any other element improving layer thermal conductivity. Such elements can be metal powder, metal felt, grid, cellular body, punched corrugations, plates, finned tubes

etc. It is important that its design provides uniformity of thermal conductivity or its greater value in a heat flow direction. It is also important to provide reliable thermal contact of heat-conducting insert with elements of construction conducting heat flow. Soldering, welding, copper or other metal coating provides it.

Bearing element of a sorber design is the container (pressure vessel), where the other sorber elements are placed. As a rule, the container is made of a seamless tube with welded bottom. Sorber should be orientated so that its long axis was normal to a gravity vector for avoiding vessel wall "swelling" in the bottom part.

3. Designing of sorbers

Sorbers can be designed in two ways: 1) all hydride is in one sorber (monoblock version) and all additional elements are in the same place; 2) hydride is in small tubes (modular version) and necessary power is achieved by increasing number of tubes. The optimum tubes diameter providing the best weight efficiency of design K_k is 20-50 mm.

MHHP functioning is possible if at least two sorbers are linked together by hydrogen line.

Description of Sorber Designs

Two types of sorbers - modular and monoblock have been designed and made for experiments. The modular sorber has tubular version (Fig. 1). Hydride powder is in the seven tubular modules united by common hydrogen manifold and surrounded by heat-insulated jacket of a heat exchanger. In the center of the module, the ceramic filter preventing removal of metal hydride and serving as a hydrogen manifold of the module is placed. Aluminium punched corrugation is utilized as the heat-conducting insert increasing heat emission from hydride to a module wall. Heating and cooling water flows between tube modules inside a jacket of a heat exchanger. Sorbers are connected through hydrogen valves to the gas main pipe linking sorbers in the common unit. High-temperature and low-temperature sorber parts differ in the length (capacity) and in metal hydride material. 7.5 kg of high-temperature metal hydride LaNi_5H_x are in a high-temperature sorber part, and 5 kg of low-temperature metal hydride $\text{MmNi}_{4.15}\text{Fe}_{0.85}\text{H}_x$ are in a low-temperature part.

The monoblock sorber has a design (Fig. 2) in which metal hydride powder is in the common cylindrical space with seven tubes for a coolant. Heat emission from hydride to walls of tubes is increased by external copper tube edges. Three ceramic filters for hydrogen flow preventing removal of hydride are placed in a hydride space. Hydrogen filters main pipes are combined by a hydrogen manifold, which is connected to the gas main pipe linking sorbers in the common unit and units with each other. Sorbers have inlet and outlet water headers and heat-insulated jacket of a heat exchanger forming the ring channel around the cylindrical shell of hydride space.

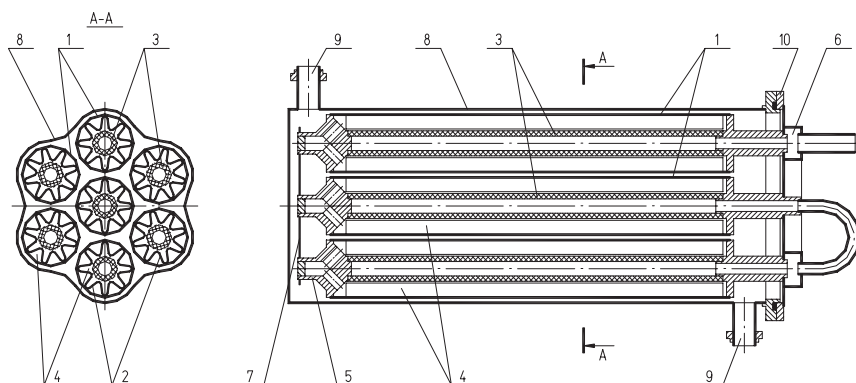


Figure 1. The MHHP modular sorber diagram: 1 - tubular case of the hydride module; 2 - corrugated heat-conducting insert; 3 - hydrogen ceramic collector-filter; 4 - metal hydride; 5 - tip of a metal hydride bed; 6 - hydrogen manifold; 7 - spacer plate; 8 - heat exchanger shroud; 9 - union; 10 - flange-cover of a heat exchanger. Heat exchanger thermal insulation is not shown conditionally.

The alloys were hydrogenated directly in sorbers.

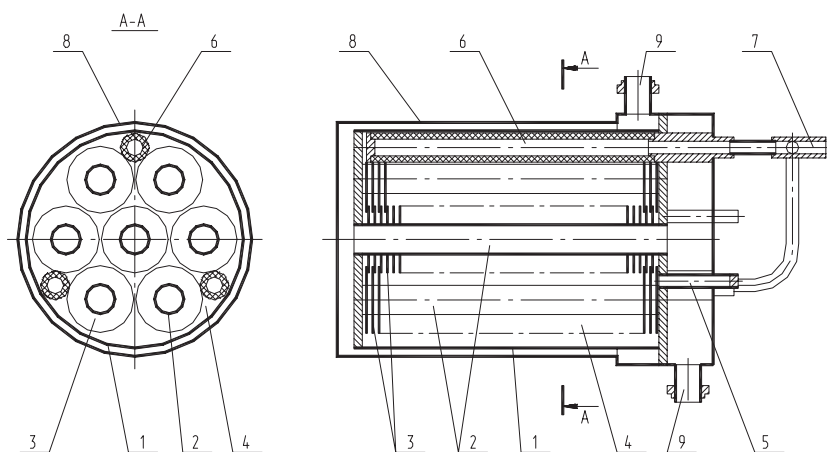


Figure 2. The MHHP monoblock sorber diagram: 1 - case of a sorber; 2 - heat exchanging tube; 3 - heat-conducting edges; 4 - metal hydride; 5 - tube with metal hydride bed; 6 - ceramic hydrogen collector-filter; 7 - hydrogen manifold; 8 - casing of a heat exchanger; 9 - union. Thermal insulation of a heat exchanger is not shown conditionally.

Evaluation of Thermophysical Characteristics of Hydride Beds

Duration and intensity of non-stationary processes heat and mass transfer in hydride beds is determined by dimensionless criteria: Fourier number - **Fo** and Biot number - **Bi**. Their relationship with physical parameters is given by formulas:

$$\begin{aligned} \mathbf{Fo} &= a \tau / \delta_{\text{char}}^2, \\ \mathbf{Bi} &= \alpha \delta_{\text{char}} / \lambda_{\text{ef}}, \end{aligned}$$

where $a = \lambda_{\text{ef}} / C_p \rho$ is coefficient of temperature conductivity of a hydride bed with characteristic size δ_{char} ; λ_{ef} – coefficient of effective thermal hydride bed conductivity, C_p – presented heat capacity of a layer; ρ – layer density; α – factor of an external heat transfer; τ – time.

To reduce time of physical processes in hydride beds it is necessary to reduce bed thickness and to increase its temperature conductivity.

Criterion Biot determines the ratio of intensity of external heat exchange processes (numerator) and effective thermal conductivity of a hydride layer (denominator). To carry out frontal chemical reactions of hydrogen sorption – desorption, small numbers Biot (**Bi** < 0.1) are preferable. Number **Bi** can be decreased by several ways: 1) decreasing of the characteristic layer size; 2) decreasing of intensity of an external heat transfer (but time of non-stationary processes is growing); 3) increasing of effective hydride bed thermal conductivity.

Thermal conductivity of plate-type reactors and reactors with corrugated insert are evaluated with use of structural two-dimensional model depending on directions of heat flow by formulas [3]:

$$\lambda_{\text{ef}} = (a/M)(a/L)\lambda_m + \{[(M-a)/L + (a/L)(\lambda_r/\lambda_m)^{-1}(1-a/L)]\lambda_h / [(M-a)/L + (a/L)(\lambda_h/\lambda_m)^{-1}]\} \quad (1)$$

for radial arrangement of elements of a skeleton and

$$\lambda_{\text{ef}} = \{[1 - (1 - a/M)^2(a/L)(1 - \lambda_h/\lambda_m)] \lambda_h / [1 - (a/L)(1 - \lambda_h/\lambda_m)]\} \quad (2)$$

for axial arrangement of repeating elements of a skeleton. Here a , M , L are sizes (a – skeleton side of square section, M – an elementary cell side, L – spacing of elements), λ_{ef} – coefficient of thermal conductivity of skeleton material.

Formulas for punched elements and for continuous elements are considerably simpler:

$$\lambda_{\text{efr}} / \lambda_h = \lambda_m / \lambda_h (1 - \varepsilon) + \varepsilon \quad (3)$$

for radial direction of plates,

$$\lambda_h = 1 / [\lambda_h / \lambda_m (1 - \varepsilon) + \varepsilon], \quad (4)$$

for axial direction, where ε – porosity determined as ratio of volume without plates to full volume. If materials with high thermal conductivity are used ($\lambda_m \gg \lambda_h$) then $\lambda_{\text{ef}} \approx \lambda_m(1 - \varepsilon)$, $\lambda_{\text{efa}} \approx \lambda_h/\varepsilon$.

By results of our experiments mean coefficient of effective thermal conductivity of powder LaNi_5 is $\lambda_{\text{ef}} = 1.25 \pm 0.05 \text{ W/(m}\cdot\text{K)}$. The porosity of powder layer was 0.5-0.55. Effective thermal conductivity of $\text{ZrCrFe}_{1.2}$ powder was 0.5 $\text{W/(m}\cdot\text{K)}$.

Values of effective thermal conductivity for a cell modeling tube sorber $\lambda_{\text{ef}} = 5 \pm 0.5 \text{ W/(m}\cdot\text{K)}$ with a corrugated foil and 1.0-1.5 $\text{W/(m}\cdot\text{K)}$ without it were found in experiments. Corrugated aluminium foil increases effective thermal conductivity of powder bed approximately 3-5 times. Value of effective thermal conductivity in mathematical model for calculations of tube sorbers was assumed to be $\lambda_{\text{ef}} = 5.8 \text{ W/(m}\cdot\text{K)}$.

Beside the problems of increase of hydride bed effective characteristics, there is a problem of coordination of external (between coolant and reactor wall) and internal (inside a reactor) heat exchanging intensity.

In general, the heat balance of MHHP heat exchanger is expressed by two equations:

$$\begin{aligned} Q_1 &= G C_p \Delta t, \\ Q_2 &= K_{\text{ht}} \Delta t_{\log} F, \end{aligned} \quad (5)$$

where F - heat exchanging surface, $\Delta t = t_{\text{out}} - t_{\text{in}}$ - difference of coolant inlet and outlet temperatures, $\Delta t_{\log}$ - mean logarithmic temperature drop.

Fluid flow and resulting difference in the temperature are bound and, consequently, to obtain the larger difference it is necessary to reduce consumption. The relationship between them is determined by designation of developed installation. For example, if necessary to have heat pick-up with certain temperature, then liquid consumption cannot be more than the certain value. Liquid consumption can be increased to remove waste heat and to accelerate preparatory processes, because at this time the temperature difference is not the limiting factor.

The heat-transfer coefficient is a function of all chain, where heat flow passes, and for one-dimensional (plane model) heat exchange between liquid and hydride bed divided by heat-conducting wall can be expressed by:

$$K_{\text{ht}} = (1/\alpha + \delta/\lambda + R + 1/\alpha_{\text{ef}})^{-1}, \quad (6)$$

where α_{ef} is the coefficient of hydride bed effective heat transfer; δ is thickness of a technological wall and λ is coefficient of its thermal conductivity, R - contact resistance on a boundary wall - hydride bed.

The coefficient of hydride bed effective heat transfer α_{ef} is proportional in general to layer effective thermal conductivity and inversely proportional to layer thickness. The analysis of this equation shows that the heat transfer coefficient is less than a smaller coefficient of heat emission and, consequently, it is meaningless to increase strongly one of them without changing the other. The experimental results show that for the soldered and diffusion welded connections of sorber case and heat-conducting insertion $R = (0.5-1.5) \cdot 10^{-5} \text{ (m}^2\cdot\text{K)/W}$. If contact between insertion and a case is tight fit, then R increases in 10-100 times and influence of contact resistance becomes comparable with influence of reduced heat emission of a hydride bed.

Joint consideration of all these equations and installation function determine strategy of designing of hydride beds and heat exchangers. Rigorous solution of transfer equations is a key to correct MHHP designing. That is why mathematical modeling of MHHP is important and necessary.

4. Application of sorbers in model sets

Brief Description of Installations

Metal hydride sorbers were in a composition of experimental installations [4, 5] based on the metal hydride heat pump. Here we shall consider in detail features of one of installations for cold generation [4] (Fig. 3) using waste heat - hot water with temperature 80-90°C - as an energy source simulator.

The main units of installation are sorbers forming two units of a metal hydride heat pump. Sorbers of the first unit are modular-type. Modules of the first unit sorbers have seven thin-walled steel tubes 25 mm in diameter. When installation works, water is run through a sorber case and flow around external surface of modules heating or cooling them.

MHHP sorbers of the second unit are monoblock-type. When installation works, coolant comes in a backlash between an external jacket and a case and then through finned tubes is removed through a branch pipe of a front manifold.

Hot water thermostat, tank of cooling water, pumps for water pumping, gas and hydraulic main pipes and control instrumentation are parts of installation beside sorbers. Units of installation operation have cyclic character. In the first half-cycle, hydrogen is absorbed by metal hydride of a low-temperature sorber. Released heat is removed by flowing water with temperature 10-15°C. Hydrogen in a low-temperature sorber comes from a high-temperature sorber, where it is desorbed due to heating by hot water.

Cold is generated in the second half-cycle. Hydrogen is desorbed from a low-temperature sorber hydride. At this time, metal hydride absorbs heat and cools water coming through a heat exchanger. Desorbed hydrogen is absorbed by high-temperature sorber metal hydride, and released heat is removed by water with temperature 10-15°C. For continuous cold generation, installation units should work with half-cycle time shift.

The other installation [5] has multipurpose function to produce superheated water at a level of 110°C or to generate cold at a level of 1.5°C with available temperature potentials of 80-90°C and 10-20°C. MHHP of installation used hydrides couple $\text{ZrCrFe}_{1.2}$ - LaNi_5 . The design of sorbers was similar to sorbers of installation in [4].

Mathematical Modelling

Mathematical model and a set of programs for computer modelling of hydride heat pumps work had been developed earlier by one of authors [6]. The system of

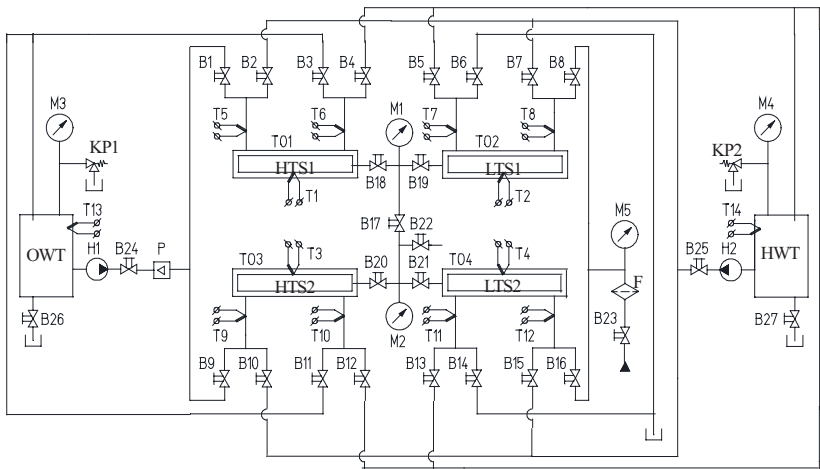


Figure 3. The diagram of cold generating installations [4]: HWT - constant-temperature chamber of hot water; CWT - tank of cooled water (liquid); HTS1, HTS2 - high-temperature sorber; LTS1, LTS2 - low-temperature sorber; TO1-TO4 – sorber heat exchanger; H1, H2 - pump; F - filter; B1 - B27 - valves; M1 – M5 -manometers; KP1, KP2 - safety valves; P - flowmeter; T1-T14 – thermocouples.

the modelling equations included the non-stationary equations of heat balance in hydride sorbers taking into consideration thermal effects during hydrogen sorption-desorption. Conditions of heat exchange of sorbers with external coolants, their real geometry and design features (materials and walls size, filters, inserts with high thermal conductivity, etc.) were taken into account. Experimental data on equilibrium isotherms in systems metal alloy - hydrogen were used during modelling. The pump operation was controlled by time of half-cycle mode setting. The time cyclogramme of MHHP operation was determined in computations: temperatures of installation elements, hydrogen contents in sorbers, hydrogen pressure, heat flows to external coolants and the main power parameters - time of cycle, developed heat power, efficiency.

Possibility of model allowed to compute and to investigate operatively influence of the various parameters determining design and functioning of a heat pump that is important both at the design stage, and for optimization of pump operating modes.

The developed mathematical model has been applied for calculation of processes in MHHP intended for vehicle air conditioning [4, 7]. Study of influence of the basic heat pump parameters (pressure of hydrogen charging, temperatures and coolant consumption, cycle time) on its power characteristics has been carried out. It was shown that the estimated data well agreed with experimental results. It was found that the developed model could be used for qualitative investigation of various parameters influence and approximate quantitative assessments.

The realized mathematical model has been also applied for computation of processes in MHHP intended to increase or decrease of a temperature level [5, 8]. It was found that to reduce discrepancy between experimental and calculated data it is

necessary to take into account hysteresis in P - C - T relationships taking place during sorption-desorption of hydrogen.

The further improvement of mathematical model can include, for example, final rate of heat transfer in sorbers, as well as influence of hydrogen sorption and desorption kinetics. Use of the model, which takes into consideration only heat and hydrogen transfer processes in sorbers' volumes, is explained by practical absence of the kinetic constants data describing processes of hydrogen sorption in the hydride forming alloys.

Results

The plot with dependence of cold generation capacity P on the change of gathered in a reception tank cooled water temperature T in working installation [4] is presented in Fig. 4. Tests of installation have shown the following results:

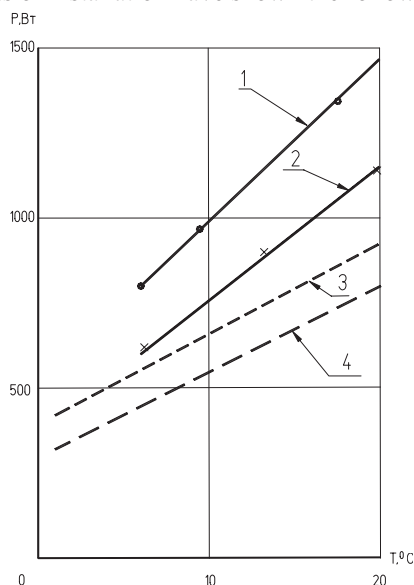


Figure 4. Dependence of cold-productivity P of units 1 (curves 1, 2 - modular sorber) and 2 (curves 3, 4 - monoblock sorber) on temperature of coolant T : $\bigcirc$ - unit 1, hydrogen content 50 g; $\bullet$ - unit 1, hydrogen content 25 g; $\times$ - unit 2 hydrogen content 25 g.

1. The maximum mean cold output is reached when cycle time is 9-11 minutes and cold water pumping is continuous. In this case the installation (with modular sorber) has 450-500 W (temperature of the cooled liquid is 0.5-1.5°C), calculated value is 500 W. For a monoblock sorber it has 300-400 W.
2. Duration of sorption processes in a couple of modular design sorbers is lower, than in a couple of monoblock design sorbers. Thus, optimum phases of charging and recharging of modular sorbers are 4-5 minutes and 6-8 minutes, respectively, and 5-6 minutes and 8-10 minutes for monoblock sorbers; it refers to 2.5 times larger heat exchange surface in modular unit than in monoblock sorbers.

The results speak in favour of the modular (tube) sorber application. The reasons of differences in sorbers operation were analyzed, they confirmed the difficulties of designing and realization of a monoblock sorber with good characteristics.

In a modular reactor, it was not possible to obtain the area of heat exchange comparable to similar area of a tube reactor at identical thermal power. Attempt to reduce the sizes of internal tubes and to increase their number in a modular reactor considerably complicates adaptability of this design manufacture.

5. Conclusions

The designing of hydride reactors is an intricate versatile thermophysical problem. It can be solved by complex approach to designing with use of mathematical modelling, technological and experimental elaboration of separate units (especially, characteristics of hydride beds). In general, the improvement of MHHP parameters may be expected after substantial improvement of hydrogen capacity of hydrides.

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OPTIMIZATION OF HYDRIDE HEAT PUMPS OPERATION

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Abstract. In article approaches to optimization of HHP operation as heat machine are planned. Optimization is directed on achievement of the maximal efficiencies, cold-productivities or levels of temperatures. Optimization of weight and the sizes of tubular sorbers are possible. The question of the coordination of a heat emission in hydride beds and heat exchangers is especially important. To increase efficiency of HHP it is possible, both by a choice of the best hydrides, and by optimum control in regime parameters of HHP. The mathematical modelling spent both a method enumeration of possibilities, and a regression procedure analysis, testifies to extreme behaviour of regime parameters of HHP.

Nomenclature

ΔH	Enthalpy of hydride formation, (J kg ⁻¹)
C_p	Thermal capacity of a sorber, (J kg ⁻¹ K ⁻¹)
Δn	Amount of active hydrogen, kg
d	Diameter, m
K_k	Factor of a design (the relation of design weight to hydride weight)
M	Weight, kg
P	Pressure, Pa
R	Radius, m
T, t	Temperature, (°C, K)
COP	Efficiency of HHP in a refrigerator cycle as the relation of a useful cold to the spent heat
HHP	Hydride heat pump

Greek symbols

α	Heat-transfer coefficient, (W m ⁻² K ⁻¹)
δ	Thickness of a hydride bed, wall, m
ε	Porosity
λ_{eff}	Heat conductivity factor of a hydride bed, (W m ⁻¹ K ⁻¹)
ρ	Density, (kg m ⁻³)
τ	Time, sec (s)
σ	Pressure, Pa

Indexes

h, m, l	Concerns to levels of temperature: high, average, low
h	Concerns to hydride

k	Concerns to a constructional material of a sorber
m	Concerns to a material of a skeleton of a heat-conducting insert
ch	Characteristic
eff	Effective

Keywords: hydride, hydrogen, hydride heat pump, modeling, optimization.

1. Introduction

After the first purposeful researches of HHP with reference to various appendices there was a question on their comparison with traditional heat machines (various refrigerators, heat pumps). It has been revealed, that for maintenance of competitiveness on weight (and cost) with usual vapour compression refrigerating machines at an identical cold-productivity of HHP should have output power on a mass unit of hydride ~ 1 kW/kg [1].

Works on increase of an overall performance of HHP were simultaneously carried out. For example, in [2] a number of the factors influencing specific output power of HHP has been considered. Properties of metal hydrides (absorbing ability, speeds of reactions, porosity of a covering, the characteristic of a heat transmission of a hydride bed) were analyzed for optimum selection. It has been shown that in pressings from powder metal hydrides gas permeability and effective specific heat conductivity of a bed λ_{eff} should be in common optimized in the certain range of a weight share of an additional heat-conducting material.

In other work cyclic operation of a metal hydride refrigerator [3] was analyzed. With the help of mathematical model for calculation of transfer processes to HHP the algorithm of definition of optimum switching of heat flows in system has been developed at given cycle time. The algorithm is constructed from a condition of achievement of the maximal refrigerating effect (real *COP*) on unit of brought heat.

There are also articles of generalizing character [4] where attempt to establish the total procedure of creation of systems of transformation of energy in pair metal hydride systems (including in HHP) is done. Alongside with questions of increase of efficiency of hydride devices are considered also questions of optimization of a hydride devices cycle.

In this article the one-stage hydride heat pump is discussed only with the purpose of optimization of some the factors influencing efficiency, specific output power and important at estimation of operation and power efficiency.

2. Efficiency and optimization of HHP operation

Ways of increase in efficiency of HHP are in detail considered in [5]. Optimization of HHP operation can be considered as an ultimate goal of increase of efficiency - creation of optimum combinations of operational characteristics. Optimization means search of an optimum (extremum) of any parameter, at which HHP has the best characteristics (on: *COP*, capacities, to a level of temperature and so forth).

Thermal energy of HHP depends on thermodynamic, thermalphysic and chemical properties of metal hydride, and also from the resulted characteristics of hydride beds in a design a sorber (reactor)-heat exchanger. At designing HHP it is

necessary to ask a question: what should be these characteristics for achievement of delivered designing tasks?

The general problems of optimization in HHP

Considering HHP as the heat machine, from the point of view of optimization of processes in HHP it is necessary for analysis to subject:

- Thermodynamic cycle of HHP (including a selection of hydrides);
- Efficiency; brought, removed capacities and energy losses;
- Laws of a structure and the characteristic of hydride beds and coverings, properties heat – and mass transfer of metal hydride bed and hydride sorber as a whole;
- The coordination of a heat emission in a sorber and a heat exchanger and between sorbers;
- Cycle of HHP operation and management of it.

3. Optimization in a selection of hydrides

At a selection of pair metal hydrides for HHP it is necessary to be guided by hydrides [4]:

- With the big absorption of hydrogen;
- With high speeds of chemical reactions in the field of working parameters of pressure and temperature;
- With an optimum combination of enthalpies and entropies at hydrides for the chosen levels of temperatures (T_h , T_m , T_l);
- With high stability of an alloy a cycling.

The choice of hydrides should be optimized under a concrete heat problem: the heat pump, a refrigerator, a heat transformer. Techniques of a choice of the hydrides can help with it using computer technologies [6].

It is necessary tell the difference between the idealized cycle of operation HHP (Carno cycle) and a real cycle. The Carno cycle has maximal COP_{id} for the chosen range of temperatures ($T_h - T_m - T_l$). The real cycle is connected to cyclic of HHP operation and always $COP_{real} \rightarrow COP_{id}$, never amount to it. For approach a Carno cycle it is necessary to reduce a hysteresis of absorption[desorption pressure and slope of curves $P-C-T$ for chosen hydrides. If in a range of working loop variables some pairs hydrides get best of them will be pair having the greatest COP_{real} .

Except for satisfaction for the above-stated requirements at a choice of hydrides it is necessary, that they had good technological (ease of activation, simplicity of manufacture) and economic parameters (availability, the low price of initial materials and expenses for manufacture).

4. Optimization of HHP design data

Optimization of a design of sorbers and hydride beds should be carried out under thermalphysic, weight and strength properties characteristics (λ , ρC_p , ρ , σ).

Weight and the size of a sorber

Use as the container for a sorber of a pipe in radius R and thickness of a wall δ allows carrying out optimization at a choice of a constructional material of a pipe. The weight and a full thermal capacity of hydride in a tubular sorber (M_h , C_h) relate to corresponding characteristics of a pipe (M_k , C_k) as follows:

$$\frac{M_h}{M_k} = \frac{\sigma_T}{\rho_k} \frac{\rho_h \varepsilon}{2P}, \quad \frac{C_h}{C_k} = \frac{\sigma_T}{C_{pk} \rho_k} \frac{\rho_h \varepsilon C_{ph}}{2P},$$

where σ_T - a yield point of a material of a pipe, P - pressure of hydrogen inside a pipe, ε - porosity of a covering of hydride in a pipe (it is supposed, that the pipe is completely filled with metal hydride). From the decision of a problem of safety connection of the sizes of a pipe is received- $\delta/R = P/\sigma_T$.

Choosing constructive materials on the greatest values of complexes σ_T/ρ_k and $\sigma_T/(C_{pk}\rho_k)$ it is possible to range constructional materials under the relation of hydride weight to design weight (so-called factor of design K_k). Under weight characteristics materials arrange in sequence - duralumin, titan, stainless steels. Under characteristics of a thermal capacity on the first place leaves the titan.

It is similarly possible to show, that optimization of radius of a pipe for achievement of its minimal weight results in the radiuses made in an interval of 25-35 mm.

Porosity, gas permeability, effective heat conductivity of a hydride bed

Effective specific heat conductivity of a hydride bed plays the basic role in a heat transfer of HHP sorbers. At work metal hydrides will disperse on fine-grained particles and form a powder bed of the micron size. The hydride powder bed tends to self-condensation that hydrogen transfer can considerably break. Heat conductivity increase by addition in powders of height heat-conducting materials (copper, aluminium). Introduction of crimps and ribs increases effective heat conductivity in one direction and does not solve the problem on increase of local heat conductivity in hydride bed. Application of metal foams and addition in hydride of powders of metals with the further pressing solves a problem of creation of a homogeneous bed. The weight part of metal has *optimum value* at a level of 0.16-0.20 weight parts (for an aluminium matrix in pressings from powder metal hydrides [2]) and provides necessary effective heat conductivity ($\sim 5 \dots 8$ W/(m·K)) and gas permeability a bed ($\sim 2 \cdot 10^{-11}$ sm²). Approximately same effective heat conductivity is provided with application of metal foams at foam porosity 0.95 (that is equivalent for copper $\sim 10\%$ weight). For foams and other structured materials with open porosity effective heat conductivity depends on porosity almost linearly. For foams on the basis of copper effective heat conductivity of all in 1.5 times exceeds heat conductivity of foam of the same porosity from aluminium, but aluminium foam more easy and has a total thermal capacity ($C_{p\rho}$) in 1.5 is lower, than foam from copper.

Heat-transfer factor

Heat exchange between a sorber and a heat exchanger in HHP should be optimized for obtaining of the maximal heat transfer factor [5]. Thus it is necessary to remember, that determining thermal resistance is the hydride bed and requirements to external heat exchangers follow from the achieved characteristics of a bed and are minor. Intensifications of a heat transfer always are necessary for achieving on the part of a hydride bed since alignment of heat-transfer coefficients on the part of a sorber and a heat exchanger reduces factor of a heat transfer twice, and essential excess of heat exchange in external in relation to a hydride bed a heat exchanger does not raise heat transfer factor above factor of an effective heat-transfer coefficient of a hydride bed. That is to say that heat-transfer factor always less than smallest of coefficients of a heat-transfer coefficient in system a hydride bed-wall-heat carrier. The heat emission of a hydride bed can be estimated under the formula $\alpha_2 = \lambda_{\text{eff}} / \delta_{\text{ch}}$ (where δ_{ch} – characteristic thickness of a bed). Having factor of an external heat emission (from the heat carrier to a wall) at a level $\alpha_1 = 10^3$ W/(m²·K) and heat conductivity of a hydride bed $\lambda_{\text{eff}} = 5$ W/(m·K), for good heat exchange it is necessary to aim to realize in a design beds with thickness $\delta_{\text{ch}} < 5$ mm. To reveal a weak place of a heat transfer and to plan ways of its elimination probably only on the basis of knowledge and the analysis of individual thermal resistance (a wall, on the part of the heat carrier, on the part of hydride). The knowledge of the general heat transfer factor in this respect gives nothing.

The special attention is required with a question on the coordination of processes of heat and hydrogen transfer in different sorbers of HHP in various stages of a cycle [5]. For example, in a refrigerating cycle of HHP the preparatory part of a cycle (compressive) occurs at pressure big on the order, than pressure in the basic (refrigerating) part of a cycle. The desire to level intensity of processes of hydrogen transfer in various stages of a cycle results in necessity qualitatively to improve processes of a heat transmission and a filtration of hydrogen in a low-temperature sorber in comparison with a high-temperature sorber. The need of extraction from hydrides of a maximum quantity of hydrogen results in necessity to extend duration of the basic half-cycle at the set general duration of a cycle [3]. The formulated problems are, as a matter of fact, optimization problems.

5. Optimization COP of HHP

The thermodynamic cycle (ideal and real) HHP is defined static and dynamic characteristics of curves of saturation of an alloy by hydrogen (pressure - concentration). Application of the hydrides having the minimal hysteresis and plateau slope of saturation increases amount useful transferable hydrogen between hydrides and expands borders of working temperatures. Realization of a real cycle always results in deterioration of its efficiency. The dynamic exchange of hydrogen between sorbers changes curves of equilibrium saturation aside their deterioration. For hydrogen flow there is a necessity to provide an obligatory difference of pressure between metal hydrides («driving force of pressure»). General efficiency of a cycle worsens.

The maximal COP

Efficiency of HHP cycle is connected to thermodynamic and thermalphysic properties of hydrides and with temperature loop variables [5]. Ways of efficiency increase are:

- Increase in an enthalpy of formation of a low-temperature alloy;
- Weight reduction of a design;
- Decrease in deviations of working temperatures from an average level of temperature T_m . It results in reduction of losses of the heat going on preheating (precooling) of hydrides;
- Application of regeneration for partial useful use of heat (cold) of preparatory stages of a cycle.

Theoretical value COP_{id} , corresponding to a Carno cycle calculates under the formula:

$$COP_{id} = \frac{T_l(T_h - T_m)}{T_h(T_m - T_l)} \leq 1.$$

Technical efficiency COP_{tech} takes into account material structure of sorbers. It aims to the maximal value at indefinitely big durations half-cycles:

$$COP_{tech} = \frac{\Delta n \Delta H_A - C_{p_A}(T_m - T_l)}{\Delta n \Delta H_B + C_{p_B}(T_h - T_l)},$$

where Δn - amount of active hydrogen in system (it is determined from equilibrium P - C - T dependences for hydrides), C_p – total (including hydride and materials of a design) a thermal capacity low-temperature A and high-temperature B sorbers.

COP achievable in a cycle

Real COP_{real} realizable in a cycle it is less than COP_{tech} . It is caused by that the amount of the active hydrogen circulating between sorbers always is less Δn . It is necessary to aim to achievement of maximal value COP_{real} , that is in turn connected to the decision of an optimum problem on loop extents (for example, about duration of its half-cycles [3]). It is revealed [3] that the optimum moment of switching in the greater degree depends on gas permeability and factor of heat exchange, than from duration of a cycle set by specifications. In turn amount of active hydrogen Δn (and, hence, and COP_{real}) strongly depends on initial pressure of hydrogen in HHP [7, 8].

6. Optimization problems of mathematical modelling

Characteristics and an overall performance of HHP depend on the big number of constructive and operational parameters. To define optimum values of these parameters in the empirical way rather difficultly. Modelling of HHP operation [6-8] allows to investigate influence, both design data, and regime parameters on efficiency of output characteristics.

The most expedient approach here – statement and the decision of corresponding optimization problems. A basis of such approach is development of

corresponding model of the most heat pump and the processes occurring in it [6]. At statement of an optimization problem it is necessary to formulate criterion of optimization that is to define those characteristics which optimum value should be achieved during optimization. So, for the HHP working in a mode of a refrigerator, it is possible to optimize it COP_{real} , a cold-productivity or temperature achievable on low-temperature hydride.

Statement of a problem of modelling and its optimization

The one-dimensional non-stationary mathematical model of HHP operation [6-8] was earlier considered. The modelling system of the equations included the non-stationary one-dimensional equations of heat balance in hydride sorbers taking into account of calorific effects at absorption/allocation of hydrogen. In computer calculations experimental data on equilibrium isotherms in systems metal alloy-hydrogen were used. HHP operation both in refrigerating [7] and in heat step-up and refrigerating cycle's [8] for the most various designs of sorbers and external heat exchangers is investigated. In calculations the time cyclogramme of HHP operation is defined: distribution of temperature of constructive elements on radius of a cylindrical hydride bed, the contents of hydrogen in sorbers, pressure of hydrogen, energy and heat rating. Research of influence of the basic regime parameters of the heat pump (pressure of a charging of hydrogen, temperatures and flows of the heat-carrier, time of a cycle) on its power characteristics and comparison of the calculated and experimental results received on modelling installations of HHP is carried out.

Enumeration of possibilities and regression technique

It is necessary to make a choice between various methods of optimization. Two methods can be considered. The first is a direct, strict method of the decision of problems in which the algorithm of optimization includes the certain strategy enumeration of possibilities. Thus restrictions on values of physical parameters are taken into account with the help of introduction of corresponding penal functions. Other way is based on use of methods regression procedure. This approach is algorithmically clearer, though is more combined in practice as assumes use of different programs. The optimized value is represented by multivariate function of arguments - changeable parameters, then after calculation of the necessary number of variants are determined unknown factors of this function, and then with the help of the standard, specially developed programs position of an optimum is determined. The basic difficulty which here inevitably will arise - definition of the most suitable kind of function and its factors. If factors enter (or can be resulted) in it by linear method at any kind of function the system of the equations for these factors will be linear. However, complexity of definition of position of an optimum depends on a kind of the given function. It is expedient to choose it so that for definition of an optimum the simple system of the equations turned out also. To these requirements the simple quadratic form of a kind

$$R = \sum_{i,k} A_{ik} x_i x_k + \sum_i B_i x_i + C \text{ satisfies. This form it is possible to lead to canonical}$$

form $R - R_0 = \sum_{i,k} D_{ik} \delta x_i \delta x_k$. Position of an optimum is defined now from system of the linear equations of a kind $\frac{\partial R}{\partial x_i} = 0$. The decision of such system any

more does not represent complexities. Actually, position of an optimum x_i^0 is determined already at reduction an canonical form. Now it is necessary to estimate, how many independent parameters can be included in consideration. The number of parameters is determined, basically, volume of the work necessary for definition of all factors. If matrix A_{ik} has dimension, for example, 4×4 , 16 variants are required, at least, to define all necessary factors. This size is not represented too big; more likely, here the greater value will be had with restrictions on dimension of systems of the linear equations. However, modern computer programs suppose rather high dimension of linear systems.

At use of functions of other kind there will be a problem of the decision of nonlinear systems, extremely complex at the big number of unknown. Thus, the algorithm of the decision of optimization problems is represented clear enough, anyway, at this first stage of statement of a problem and development of algorithms. On the basis of the submitted reasons basically schematic circuit of computer optimization programs have been developed. However they demand independent consideration here again because of lack of a place their decision is not resulted. Dependence of efficiency of installations from HHP was defined enumeration of possibilities.

Influence detection of the basic regime parameters from a point of view of optimum values search

For the developed mathematical model of HHP alternative calculations have been carried out with the purpose of search of optimum values of regime parameters for concrete installations [7, 8]. It has been determined, that there are optimum initial pressure in sorbers of HHP, optimum temperature modes (at levels of temperatures T_h , T_m , T_l), providing the maximal efficiency. Optimization of control by HHP operation it is possible to achieve optimum characteristics of capacity and to choose necessary duration of a cycle of HHP. Control of the hydride heat pump is its essential part and as show the carried out calculations [7, 8], essentially influences efficiency of its operation. Experimental results basically have proved mathematical calculations.

7. Conclusions

Optimization of various parameters and operating modes HHP is possible, but the general increase of capacity of HHP is connected, first of all, to improvement of hydride properties.

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AUTONOMOUS WIND-HYDROGEN STATIONS

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Abstract. This work deals with a concept for the development of the autonomous wind-hydrogen stations transforming the primary energy of wind into environment-friendly energy carrier, hydrogen, and oxygen as a by-product.

The main idea is in the availability to use a substandard electric power generated by a wind power station for the production of the commercial hydrogen and oxygen by the electrolysis of desalinated water. The proposed way of its realisation includes the application of an advanced wind turbine combined with a novel high-pressure alkaline electrolyser which directly supplies the generated hydrogen and oxygen into storage systems, bypassing the compression stage.

Keywords: autonomous wind-hydrogen station (AWHS), wind power station (WPS), high-pressure alkaline electrolyser (HPAE)

1. Introduction

The increasing deficit of the natural hydrocarbon fuels, as well as the growing global environmental problems, called forth the worldwide rise in the activities related to power generation from renewable energy sources, like wind, sun, tidal and sea wave power, geothermal energy, etc. In turn, the increased attention is paid to the usage of hydrogen as an abundant, highly efficient, technologically flexible and ecologically clean synthetic energy carrier.

The major drawback of the renewable energy systems is, at least now, in too high specific energy investment costs. For example, nowadays the paying-back term of the industrial solar panels is compatible with their operation lifetime, and, in some cases even exceeds the latter. That is why the solutions allowing to utilise the renewable energy by the more efficient way are in the great demand.

We consider wind as a prospective primary energy source, to yield an idea of combining a wind-electric power plant and a hydrogen-producing electrolyser into

the unified complex [1]. This idea is realising now by many researchers and engineers in Europe and US [2,3].

This work is devoted to the development of the concept of the autonomous wind-hydrogen stations, where the primary energy of wind is transformed to substandard electric power and, further into commercial hydrogen and oxygen by the electrolysis of desalinated water.

2. Concept of the AWHs development

According to the main idea, the autonomous wind-hydrogen station (AWHS) should be adapted to the conditions when a single consumer of the produced electric power is an electrolyser, which does not require standard stable parameters of power supply for its normal operation. To realise this idea, two main problems have to be addressed in the course of the development of the AWHs.

The first one concerns the layout of the wind power station (WPS) to be efficient in the wide range of wind speeds, safe and reliable, simple in its making and operation, and having low cost. The basic engineering solution envisages the wind turbine where the wind rose mechanism provides the passive orientation of the turbine's head with the wind. The blades of the turbine are asymmetric on their weight and aerodynamics, to provide the automatic control of the blades slewing angle by a simplified controlling system. The distinguishing feature of such a WPS, as compared to the "classic" layout mainly used worldwide (by Vestas, Enercom, Nordex, Micon, Jacobs, Sudwind, etc.), is its simplicity and low cost, since the load of the WPS is the electrolyser only. Moreover, this solution also provides the safe operation, by the usage of the asymmetric blades which, when wind speed exceeds the rated one, are turned to the position with the negative angle of attack.

The second problem is related to the proper selection of the electrolyser which should provide reliable and efficient operation under conditions of unstable in voltage and current power supply.

The modern alkaline and PEM electrolysers are characterised by productivity from few tens litres to several hundreds cubic metres per hour at output pressure 1 to 50 atm. Some electrolysis plants can produce up to 4 tons of hydrogen under pressure of 7 atm per a day. The typical current density and efficiency are of 1.6 A/cm² and 60–75% (power consumption 4–5 kW·h/Nm³ H₂), respectively. Nowadays, high operating pressure, up to 200 atm, is used to increase the efficiency of electrolysers. Also, the electrodes covered by noble metals and advanced electrolytes are applied. In the future it is possible to increase the efficiency of the electrolysers up to 80–90% [4–6].

The main drawback of the alkali electrolysers is that they require rather stable operation conditions, i.e. stationary operation mode, being loaded by 20–100% of their nominal productivity. Otherwise, the service life of the electrolyser is significantly reduced. The PEM electrolysers are less sensitive to the variations in their load, but they are 5–7 times more expensive and require high purity of the supplied water for normal operation.

We have developed a new type of the alkaline electrolyser whose operation does not require a membrane separating the chambers where evolution of hydrogen and oxygen gases takes place. The most important distinguishing feature of the electrolyser, as compared to the convenient solutions, is in the presence of only one gas evolution

chamber and two-stage operation of the setup [7,8]. At the first stage hydrogen is evolved on the negative gas-evolution electrode, while in the positive, active, electrode the electrochemical oxidation reaction being not accompanied by oxygen evolution takes place. The amount of hydrogen generated is determined by the electrochemical capacity of the active electrode which is charged during the first stage. After its completion, the polarity of the electrodes is reversed, and the second stage starts, being accompanied by the discharge (reduction) of the negative active electrode and oxygen evolution on the positive gas-evolution electrode. After completion of the second stage, the first one is started again, i.e. the operation cycle is repeated.

By the usage of special gas-distributing system, the generated oxygen and hydrogen are collected in the separate containers. Since the electrolysis cell does not contain separating membranes, it has much less limitations as to its output gas pressure than for the conventional layouts. In practice, these limitations are only caused by the solubility of gases (hydrogen and oxygen) in the electrolyte, as well as by the strength of the containment. We have reached the output gas pressure up to 700 atm in some special experimental tests, and up to 150–200 atm in the prototype and small-batch electrolyzers developed in the course of realisation of this solution. These units are characterised by the following performances:

- Water consumption for the production of 1 Nm³ H₂ is about 840 ± 20 g.
- Maximum voltage drop on the cell is less than 1.5–1.6 V. Note that at the beginning of the each stage the voltage drop is much lower that significantly reduces the consumed electric power.
- The power consumption for the production of 1 Nm³ H₂ does not exceed 4.1–4.3 kW·h. This value mainly depends on the required purity of the delivered hydrogen and the design features of the electrolytic cell.
- The electrolytic cell is reversible that allows to use it both as an electrolyser and as a fuel cell [9].

The further improvements of the described above solution of the high-pressure alkaline electrolyser mainly concern the optimisation of the composition and preparation technology of the active electrodes. So, the application of the electrochemically-deposited materials for making the active electrodes allows to significantly reduce the voltage drop (to 0.6–1.5 V, as compared to 1.7–2.2 V which is specific value for the conventional low-temperature electrolyzers). In turn, the increase of the output pressure to 200 bar makes it possible to increase the operation temperature to 150 °C that results in the reduction of the overpotential. It increases the efficiency reducing the power consumption for the production of 1 m³ H₂ and 0.5 m³ O₂ to 4.1 kW·h.

The novel high-pressure alkaline electrolyser is characterised by high safety and reliability, simplicity in making and operation, low requirements to the stability of the consumed electric power, and the efficiency 30% higher than similar electrolyzers of the conventional layout. Moreover, it directly supplies the generated hydrogen and oxygen into gas-cylinder storage systems, bypassing the compression stage.

The integration of the advanced wind power station and the novel high-pressure alkaline electrolyser makes it feasible to develop an efficient autonomous wind-hydrogen station (Figure 1). The station has estimated power of 200 kW, and, being operated at rated conditions, can produce ~ 100 kg (1100 m³) of hydrogen per a day. It corresponds to

300 litres of petrol in energy equivalent and results in the reduction of CO₂ emissions by 800 kg. The specific values of performances of the AWHs will be dependent on the regional climate conditions.

3. Conclusions

The concept of simple, reliable and efficient autonomous wind-hydrogen station transforming wind energy into commercial hydrogen and oxygen by the integration of the advanced wind power station and the novel high-pressure alkaline electrolyser is proposed. The realisation of the proposed concept would significantly contribute into further solution of worldwide energetical and ecological problems, by the implementation of renewable energy sources and hydrogen as energy carrier.

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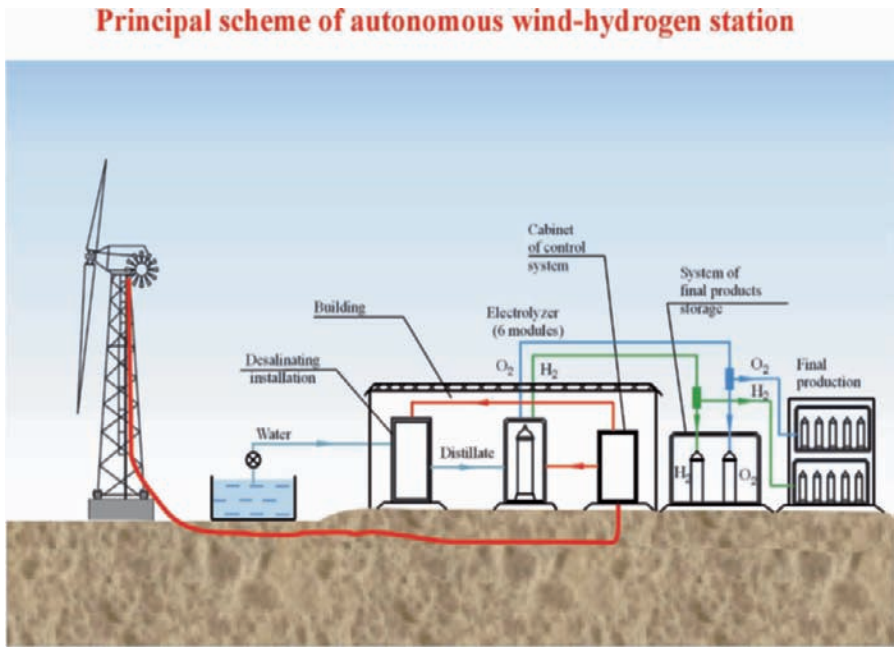


Figure 1.

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